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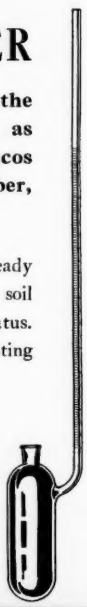

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CHEMICAL AND PHYSICAL CHANGES IN SOIL COLLOIDS WITH ADVANCING DEVELOPMENT IN ILLINOIS SOILS[1]

R. H. BRAY[2]

Illinois Agricultural Experiment Station

Received for publication May 11, 1936

This paper is based on a chemical study of soil development being carried on by the agronomy department, Agricultural Experiment Station, University of Illinois. Part of the study includes five profiles varying in profile development and weathered condition. These five profiles were chosen for study because they represent successive stages in the development of the poorly drained prairie soil developed on Peorian loess of Wisconsin age. This development took place under a humid temperate climate now characterized by warm summers and cold winters and by a rainfall of 36 to 40 inches.

The five successive stages of development are represented by Stage 1, Hartsburg silt loam [called "Monmouth" in previous papers (1, 2)]; Stage 2, Grundy silt loam; Stage 3, Harrison silt loam; Stage 4, Putnam silt loam; and Stage 5, Cisne silt loam (9). Table 1 gives profile descriptions of Stages 1, 3, and 5. A chemical study, which supports the interpretations given in this paper, has also been made of Stages 2 and 4. The profiles were chosen in an approximately straight line to the southeast of the Mason County sand area, the main source of the loess. The distance from the Hartsburg profile to the Cisne profile is approximately 60 miles.

Within this short distance the depth of the Peorian loess varies from more than 300 inches near the source of the loess in the Hartsburg silt loam to about 50 inches in the Cisne silt loam. The underlying material is Illinoian gumbotil. This variation in development and its association with the variation in loess depth and distance from the source of loess were established by R. S. Smith and E. A. Norton through field studies. Chemical studies of these profiles have been discussed in previous papers (1, 2). Horizon descriptions by E. A. Norton and colloidal material smaller than 1 μ, organic carbon, and inorganic carbonates determined by Eric Winters are included as part of the profile descriptions given in table 1.

The profile descriptions show that this Hartsburg-Cisne developmental series is just such a developmental series as described by Marbut (8). Surface parent material, topography, vegetation, and climate are approximately similar

[1] Contribution from the division of soil fertility, department of agronomy, University of Illinois. Published with the approval of the director of the experiment station.

[2] Assistant chief in soil survey analysis.

TABLE 1

Profile descriptions of Stages 1, 3, and 5

NUMBER	HORIZON	DEPTH	DESCRIPTION	COLLOIDS <1μ*	ORGANIC CARBON*	$CaCO_3$ EQUIVALENT*
		inches		*per cent*	*per cent*	*per cent*
			Stage 1†			
14034	Ia	0–8	Black laminated silt loam	22.3	2.53	0
14035	Ib	8–14	Subangular particles—clayey silt loam	25.3	1.46	0
14036	Ic	14–18	Transition to IIa. Subangular—coated drabbish brown	31.0	0.86	0
14037	IIa	18–24	Prisms 1–1½ inches. Coated drabbish brown. Inside color yellowish gray. Slightly compact clay loam	31.6	0.67	0
14038	IIb	24–31	Similar to IIa. Less compact. Reddish yellow splotches	26.3	0.41	0
14039	IVa	33–40	Calcareous (secondary and primary) friable silt, pale yellowish gray	17.0	0.40	8.2
14040	IVb	40–52	Similar to IVa. Splotched reddish yellow	10.7	0.30	17.0
14041	IVc	52–64	Very friable. Similar to IVb. Small land snail shells	8.0	0.25	24.0
14042	IVd	64–72	Very friable. Similar to IVc. Large lime concretions up to 5 inches long	7.0	0.25	27.0
			Stage 3‡			
14065	Ia	0–7	Laminated, friable, grayish brown silt loam	15.4	1.89	
14066	Ib	7–13	Very small particle structure. Friable	17.6	1.66	
14067	Ic	13–18	Transition. Prisms begin. Particles coated brownish black, heavily gray specked	25.6	1.18	
14068	IIa	18–25	Prisms 1½ to 4 inches. Coated brownish black. Compact and medium plastic	38.4	0.76	
14069	IIb	25–31	Coatings more drabbish than above. Inside color lighter	35.3	0.49	

* Determinations by Eric Winters.

† Type: Number 44 Hartsburg silt loam (formerly "Monmouth" and so called in former papers).

Location: T 18 N, R 7 W, Section 6, NE 1/4, NE 40, NE 10. Menard County.

Topography: Slight slope to NE. Calcareous at 33 inches—water table at 70 inches. Vegetation originally prairie—now roadside sod.

Sampled by: E. A. Norton and R. H. Bray 8–3–32.

The profile is calcareous loess to 190 inches, showing little difference from IVc and IVd. Not studied below 190 inches. IVd has slightly more red color, indicating some Fe_2O_3 accumulation due to drainage conditions.

‡ Type: Number 127 Harrison silt loam.

Location: T 13 N, R 2 W, Section 6, NE 1/4, NE 40, SE 10. Christian County.

Topography: Very gentle slope to north. Vegetation originally prairie—now roadside sod.

Sampled by: R. H. Bray and E. A. Norton 9–16–32.

Loess 74 inches deep. Carbonates absent.

TABLE 1—*Concluded*

NUMBER	HORIZON	DEPTH	DESCRIPTION	COLLOIDS <1μ*	ORGANIC CARBON*	$CaCO_3$ EQUIVALENT*
		inches		*per cent*	*per cent*	*per cent*
			Stage 3‡—Concluded			
14070	IIc	31–38	Slightly compact and plastic. More yellowish color than above	29.4	0.34	
14071	IIIa	38–48	Transition. Prisms absent. Very slightly compact. Numerous dark brown pellets	22.8	0.23	
14072	IIIb	48–60	Very friable. Gray splotched with yellow	16.1	0.08	
14073	IIIc	60–68	Light gray splotched with yellow. Very friable	15.4	0.08	
14074	IIId	68–74	Darker colored loess on weathered till	14.5	0.14	
			Stage 5§			
14083	Ia	0–8	Brownish gray friable silt loam. Laminated	12.0	1.51	
14084	Ib	8–14	Light brownish gray. Friable	12.2	0.77	
14085	Ic	14–21	Ashy gray layer. Numerous iron concretions at 20½ to 21 inches. No transition horizon	9.0	0.32	
14086	IIa	21–31	Prismatic. Heavily gray coated. Very compact and plastic. Inside color yellowish gray with yellowish brown splotching	42.0	0.53	
14087	IIb	31–38	Less coating. More splotching than IIa	37.1	0.37	
14088	IIc	38–46	Less compact and plastic and more gray than IIb	28.8	0.22	
14089	IId	46–53	Heavily iron stained. Slightly compact and plastic	25.8	0.24	
14090	Transition	53–56	Friable. Dark gray. Probably mixed with underlying till. Transition horizon	23.0	0.24	

§ Type: Number 2 Cisne silt loam (U. S. Bureau = Corey).
Location: T 7 N, R 1 E, Section 4, NE 1/4, NE 40, NE 10. Fayette County.
Topography: Slope very gentle to NE. Vegetation originally prairie—now roadside sod.
Sampled by: R. S. Smith, E. A. Norton, and D. C. Maxwell.
All of profile highly acid. True III horizon not present.

for all profiles. They vary, however, in depth of loess, with the result that the shallower profiles at a distance from the loess source are more directly underlain by the impervious Illinoian gumbotil, which has had a great influence on the relative rate of development. Variation in rate of development appears to be the major variable which has created this developmental series especially with regard to the weathered and leached condition of the colloids and the amount of colloid movement (illuviation). The leached condition of the profiles is indicated by the degree of saturation of the base-exchange complex, with bases, which is from 87 to 100 per cent for the Stage 1 profile from the

surface to 72 inches and from 16 to 78 per cent for the Stage 5 profile from the surface to 56 inches.

Another group of three samples represents the change of a shale into a soil material and is composed of a sample of Maquoketa shale, which was the parent material of the Wisconsin drift on which the soil developed; a sample of the IVb horizon of Clarence silt loam, which is still high in original carbonates; and a sample of the IIb, which is carbonate-free. These last two samples represent successive stages of the change in the shale when exposed to soil weathering conditions. The IIb horizon sample was taken from 20 to 25 inches, and the IVb horizon sample, from 33 to 40 inches. They were collected by R. S. Stauffer in Ford County; location: Township 23 North, Range 14 West, Section 15, SE 1/4, SE 40.

The horizon nomenclature used is that of Norton and Smith (10), with Roman numerals substituted for capital letters. In this system horizons I and II are similar to the A and B of the Russian system. Horizon III is leached of carbonates and has partially decomposed to form secondary materials. According to the definition of horizon III, the secondary minerals present have formed in place. Horizon IV contains carbonates but is partially leached and has weathered to form some colloidal material. Horizon V is practically unweathered parent material. Subhorizons are designated by small letters.

The present study is restricted to the colloidal fraction of the soil and will take up the physical and chemical changes which have occurred *within* the colloidal fraction due to the processes connected with weathering and soil development. In addition, an interpretation of the reasons for these differences, both physical and chemical, is given.

In previous papers (1, 2), the writer established the fact that the development of horizon II, the accumulative horizon, in the poorly drained loess prairie soils of Illinois was due principally to migration of the finer colloidal material from horizon I, the surface horizon, and its deposition in horizon II through physical means involving no chemical change. Since the finer colloidal material has a different composition in certain respects from that of the coarser colloidal material, chemical (as well as physical) changes corresponding to these differences in composition and size will occur in both horizons I and II. The changes in horizon I will be due to loss of the finer colloidal material, whereas the changes in horizon II will be due to the gain of the finer colloids. In addition to this kind of chemical and physical change within the profile, the physical breakdown of the coarser colloids to finer colloids can be shown to have an effect on the chemical composition of the respective size fractions within a given horizon, although chemical differences due to purely chemical decomposition or alteration are usually the most significant except for certain conditions which will be discussed later.

The colloid study is based on a method of study of clays described by Bray, Grim, and Kerr (3) in which the colloid smaller than 1 μ in size is fractionated

into fractions approximating 1.0 to 0.1 μ, 0.1 to 0.06 μ, and less than 0.06 μ in diameter. These fractions, called "coarse," "fine," and "superfine," respectively, as well as the non-colloidal residue, are then analyzed and subjected to petrographic and X-ray studies. This paper will be restricted to the physical and chemical data obtained by the foregoing method. Obtaining complete chemical data on these three size fractions within each horizon, from horizons varying in weathered condition and development, permits interpretations of soil development which are not possible by the usual methods of study.

The base-exchange capacity determinations were made on the dried colloid. The weighed colloid was leached with slightly alkaline ammonium acetate, than with neutral ammonium acetate, followed by a neutral absolute alcohol wash. The replaceable ammonia was determined by distillation and titration. This is essentially the method proposed by Kelly (7). The inorganic exchange capacities were run by boiling the colloids in 15 per cent H_2O_2 previous to the aforementioned determination. With the exception of the superfine colloid of the surface soils, the total capacities do not differ greatly from the inorganic capacities; consequently, this decomposition of the organic exchange capacity involves only a small correction.

In both groups of soils previously mentioned, the unweathered or almost unweathered parent material is included. Sample 14042 from horizon IVd of Hartsburg silt loam is practically unweathered loess, representing the material from which the five profiles were formed; the shale sample D.S. 43 represents the unweathered parent material of the Clarence silt loam horizons. The sequence of decomposition or weathering is from the parent material up through the profile to the surface horizon within a given profile. Within a profile it is therefore possible to compare the colloids of horizons as to change in weathered condition or decomposition.

The tracing of the changes which occur with advancing development within the colloidal fraction of the soil requires that the colloids be arranged in their approximate stages of development. In the Hartsburg-Cisne developmental series we are dealing very obviously with a developmental series such as that described by Marbut (8). In this particular case the profiles are already naturally arranged in their order of relative development, which follows the straight line to the southeast of the source of loess. The variations expressed along this line are mainly variations in stages of development, although some differences in kind of development appear to be present. Any differences in kind of development, however, have to do with the type of profile development rather than with the nature of the colloidal material formed as indicated by a study of other Illinois profiles.

It is therefore possible to arrange the colloids of similar horizons in their relative order of development according to the distance of the profile from the loess source. When, however, a general study of all the horizons of all profiles is being made, other criteria must be used. For example, although the colloidal material of horizon Ia of the Harrison silt loam (Stage 3) is relatively

more developed than the Ia of the Hartsburg silt loam (Stage 1), it does not follow that the colloidal material of horizon IIIa of the Harrison is more developed than the Ia of the Hartsburg. We must recognize that variations in development within individual horizons occur and that the stage of development of the profile as a whole does not fix the stage of development of the of the individual horizons. This was early recognized by Glinka, who speaks of individual horizon development (5).

In arranging the colloids in the order of their relative development, recognition has been given not only to the relative development of the profile but also to their chemical values and to the relative development of the horizons within a profile. Chemical differences brought about by natural fractionation within the profile caused by colloid movement have also been considered as well as the chemical differences caused by physical breakdown of the coarse colloid fraction (1, 2, 4). This arrangement is, therefore, based entirely on the judgment of the writer as formed from the foregoing considerations and may not coincide with the ideas of other workers in this field. On the correctness of this arrangement, however, depends the value of the interpretation of the data. The colloids in tables 2, 3, 4, and 5 are therefore arranged in order of their relative development as individual horizons, although their profile stage of development is also given.

In former papers (1, 2) reference was made to the fact that the chemical, petrographic,[3] and X-ray data[4] on the colloid fractions show that the colloidal fraction is essentially a mixture of sericite-like and beidellite-type minerals with some quartz and organic matter. The sericite-like mineral is a K_2O, MgO mica (3, 6), and the beidellite-type material is represented largely by a mineral corresponding to $Rep_2O \cdot MgO \cdot (Al_2O_3)_6(SiO_2)_{18}(H_2O)_{15}$ where Rep stands for replaceable bases and iron can partially replace aluminum (2). This association of a K_2O, MgO mimeral with a MgO, base-exchange mineral and the weathering of the former to form the latter explain in large part the chemical data obtained in the developmental series studied.

PHYSICAL CHANGES OF THE COLLOIDS IN THE HARTSBURG-CISNE DEVELOPMENTAL SERIES

The study of the physical changes of the colloids with advancing development is confined chiefly to the amount and distribution of the coarse, fine, and superfine size fractions. As has already been shown by the writer (1, 2), the development of horizons I and II is due to the formation and movement of very fine colloidal silicates (the beidellite-type materials). The chemical alteration of one mineral to form another need not necessarily involve a change in size of the altered particle. We have, therefore, the possibility that physical breakdown of the larger colloidal particles, whether altered or not, is involved in development.

[3] Petrographic data by R. E. Grim.
[4] X-ray data by P. F. Kerr.

There is also the further possibility that the product formed by the alteration is more readily broken than the mineral being altered. Physical weathering of the colloid would in such a case effect a partial size separation of the altered from the unaltered forms. Subsequent fractionation of the whole colloid would then effect a separation, and the resulting size fractions would vary correspondingly in composition, compared to their composition before physical weathering occurred.

TABLE 2

Variation in chemical composition of the coarse colloid with development

NUMBER	HORIZON	STAGE OF PROFILE DEVELOPMENT	RELATIVE DEVELOPMENT OF HORIZON	BASE EXCHANGE CAPACITY	K_2O§§	MgO	Fe_2O_3	H_2O^-††	H_2O^+‡‡	SiO_2/R_2O_3	ORGANIC MATTER
				*m.e.***	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*
DS43C	Shale§	0	1	13	6.43	3.59	8.41	0.87	6.35	2.90	....
14042C	IVd	1	2	47	2.40	2.36	15.05	6.82	....	2.80	....
14039C	IVa	1	3	48	2.15	2.24	10.56	4.34	....	3.23	....
14037C	IIa	1	4	62	1.74	2.01	8.42	4.48	7.42	3.12	2.18
14073C*	IIIc	3	5	52	1.75	1.63	11.05	2.47	8.11	3.07	0.58
14071C*	IIIa	3	6	67	1.52	1.81	10.67	2.85	8.04	3.11	0.88
14068C*	IIa	3	7	68	1.25	1.58	8.62	4.13	8.94	3.15	1.47
14034C	Ia	1	8	42	2.17	1.55	6.38	4.66	6.17	3.52	7.18
14089C*	IIc	5	9	52	1.46	1.40	8.96	3.40	8.60	3.00	0.59
14086C*	IIa	5	10	54	1.27	1.25	8.59	3.44	8.81	3.07	1.04
14065C	Ia	3	11	46	2.39	1.15	5.78	2.98	7.01	3.79	4.78
14083C	Ia	5	12	31	1.74	0.81	5.56	2.60	7.05	4.13	4.82
8090C	II†	?		32	3.91	1.89	5.38	4.36	5.79	3.92	3.30
Kan. C	II‖	5–6		38	1.89	0.98	4.38	2.01	6.66	4.06	0.41
6278C	III‡	?		20	0.30	0.25	12.64	2.20	13.39	1.47	....

* Not fully fractionated.

† Filmore silt loam. Obtained through the courtesy of Prof. F. H. Hayes.

‡ Cecil clay loam. Obtained through the courtesy of Dr. H. G. Byers.

§ Maquoketa shale.

‖ The B of the Kansan glaciation from Fairfield, Iowa. Supposedly a much more mature B than any other studied in this region.

** Per 100 gm.

†† H_2O below 110°C.

‡‡ H_2O above 110°C.

§§ All bases are non-replaceable.

With increasing development one might expect the K_2O in the coarse colloid of the surface soil to decrease as a result of chemical weathering, and one would expect the surface coarse colloid to be a more weathered product both chemically and physically than the coarse colloid in horizon II. Acutally we find that the K_2O content of the surface coarse colloid in horizon I of the Hartsburg

silt loam (14034C, table 2) is higher than that of the coarse colloid from horizon IIa (14037C) and lower than that of 14065C, the coarse colloid of Stage 3.

This apparent anomaly, showing a rise instead of the expected lowering of the K_2O, is readily explained on the basis of preferred physical weathering. The lower horizons are not so subject to physical weathering as the surface horizons, hence more coarse colloid occurs in horizon II(2). Furthermore, the physical weathering occurring in the surface appears to break down the more easily broken beidellite-type materials containing no K_2O and leave the mica relatively more concentrated in the coarse colloid size fraction in the more weathered stages of development.

Figure 1 illustrates our concept of the differences, both physical and chemical, that can result from purely physical weathering of the coarse colloid. This

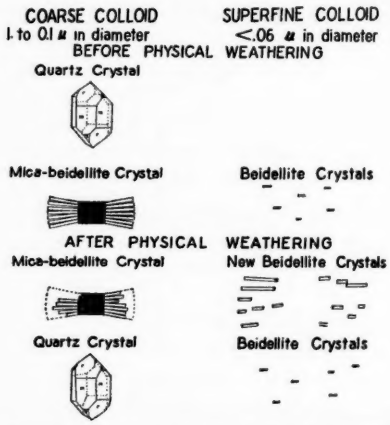

FIG. 1. PHYSICAL AND CHEMICAL DIFFERENCES THAT CAN RESULT FROM PURELY PHYSICAL WEATHERING OF A COARSE COLLOID

concept is partly based on the fact that the coarse colloid gives the sericite-like X-ray pattern and petrographic data whereas the superfine colloid gives the beidellite-type pattern and data (1). Figure 1 is used purely as an illustration of how a chemical change within a size fraction can occur by physical weathering: it is not meant to imply that the diagram shows exactly what happens. The black mineral in figure 1 represents a mica-type mineral which has produced the beidellite-type mineral through direct alteration, forming the coarse colloid particle as illustrated. The mica loses its potash and part of its magnesium, taking up water in the process, and forms a beidellite-type mineral containing some magnesium and no potash but possessing base-exchange properties. Before physical weathering the beidellite is still attached to the mica; after physical weathering considerable of the beidellite but only a very small part of the mica is broken off, becoming part of the superfine (and fine)

fraction. This will increase the K and Mg content of the coarse fraction and decrease its base-exchange capacity, and where quartz is present, as illustrated, the relative quartz content will be increased.

That these chemical changes actually occur in nature has already been established by the writer (1, 2). Table 2 shows that the 14034C surface colloid is higher in K_2O and lower in base-exchange capacity than 14037C, which indicates more of the beidellite-type material in 14037C. The 14065C sample from the surface of Stage 3 is also correspondingly higher in K_2O, although similar in base-exchange capacity, and lower in MgO, showing an increase in K_2O content with advancing development between profiles similar to that shown between the I and II horizons within a profile. We have also produced these same changes mechanically in the laboratory, reducing the base-exchange capacity of the 14037 coarse colloid from 62 to 41 m.e. per 100 gm. while increasing the K_2O from 1.74 to 2.89 per cent and decreasing the water from 11.9 to 9.5 per cent. This was accomplished by repeated fractionations and working or puddling of the colloid while in a plastic state. Other experiments indicate that no increase in the base-exchange capacity of the whole mass is caused by such manipulations. It should be emphasized that this physical weathering produces no change in the chemical composition of the mass and that it is only by subsequent fractionation and analysis of the size fractions that changes in chemical composition within the size fractions are revealed.

CHEMICAL DIFFERENCES IN THE HARTSBURG-CISNE SERIES COLLOIDS CAUSED BY ADVANCING DEVELOPMENT

Chemical differences between colloids in this developmental series can be caused, not only by chemical weathering, but also by physical weathering as has been illustrated and by colloid movement as mentioned in the introduction.

Table 2 shows the combined effect of these factors on the chemical composition of the coarse colloid fraction. Three colloids from other regions, in addition to those of the Hartsburg-Cisne and the shale series, are included for comparison. The general tendency is for the K_2O, MgO, and Fe_2O_3 to decrease with advancing development and for the $\frac{SiO_2}{R_2O_3}$ ratio to increase. The effect of physical weathering is illustrated by samples 14034C, 14065C, and 14083C. Although these samples represent horizon I of Stages 1, 3, and 5, respectively, it is the Stage 3 coarse colloid (14065C) which is highest in K_2O. With advancing development, however, chemical weathering becomes dominant and 14083C is lower in K_2O than either Stage 1 or 3. The effect of physical and chemical weathering is also illustrated by the increase in $\frac{SiO_2}{R_2O_3}$ ratio of these samples from 352 to 4.13, which results mainly from the fact that the quartz remains unbroken whereas the beidellite-type mineral or minerals being formed by chemical weathering break up and go into the finer fractions. The effect of physical weathering is not shown so strikingly in the

horizon II or III colloids, because most of them are not completely fractionated. The organic matter content is highest in horizon I and where similar horizons are compared it decreases with advancing development. The base-exchange capacity at first increases with advancing development. This is followed by a decrease in the later stages.

The corresponding superfine colloid values are given in table 3. They are arranged in the same order as are the coarse colloids of table 2. Since the superfine colloid is a result of the physical and chemical weathering of the coarse colloid, as well as of the non-colloidal soil minerals, certain differences

TABLE 3

Variation in chemical composition of the superfine colloid with development

NUMBER	HORIZON	STAGE OF PROFILE DEVELOPMENT	RELATIVE DEVELOPMENT OF HORIZON	BASE EXCHANGE CAPACITY	K_2O§	MgO	Fe_2O_3	H_2O^-†	H_2O^+‡	SiO_2/R_2O_3	ORGANIC MATTER
				*m.e.**	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*
DS43S	Shale	0	1	27	6.25	3.74	6.44	2.77	6.19	3.23	....
14042S	IVd	1	2	64	1.34	2.62	14.32	6.18	....	2.90	....
14039S	IVa	1	3	88	0.96	1.89	11.39	6.06	8.51	2.97	2.85
14037S	IIa	1	4	81	0.89	1.71	10.66	6.30	9.72	2.99	3.91
14073S	IIIc	3	5	84	0.73	1.63	10.51	4.44	10.02	2.69	1.63
14071S	IIIa	3	6	84	0.71	1.67	10.31	5.89	9.19	3.08	2.81
14068S	IIa	3	7	84	0.59	1.49	8.69	5.25	11.43	2.88	4.26
14034S	Ia	1	8	..	0.76	1.29	7.99	7.06	8.57	3.03	23.22
14089S	IIc	5	9	70	0.73	1.15	9.91	6.00	11.10	2.93	1.92
14086S	IIa	5	10	68	0.80	1.14	9.91	6.48	11.89	2.78	3.21
14065S	Ia	3	11	..	0.29	0.95	6.17	6.17	8.05	2.87	39.62
14083S	Ia	5	12	47	0.44	0.59	4.25	5.96	10.69	2.53	36.10
8090S	II	1		73	1.64	1.84	8.92	9.83	8.23	3.22	2.03
Kan.S.	II	5–6		77	0.34	1.14	8.16	5.42	10.02	2.70	0.57

* Per 100 gm.

† H_2O below 110°C.

‡ H_2O above 110°C.

§ All bases are non-replaceable; replaceable bases are not included in the values given.

in composition can be expected. The K_2O values are greatly reduced in the superfine fractions while the MgO values are only slightly lower. The trend with respect to maturity, however, is the same for K_2O, MgO, and base-exchange capacity as that found in the coarse colloid. Iron, organic matter, and water are decidedly higher in corresponding superfine fractions. In contrast to the coarse colloid, the $\frac{SiO_2}{R_2O_3}$ ratios decrease with advancing maturity.

Data for the fine colloids are not included but are more nearly similar to the superfine colloid values than to the coarse colloid values.

TABLE 4

Variation in chemical composition of the size fractions with development*

NUMBER	HORIZON	STAGE OF PROFILE DEVELOPMENT	BASE EXCHANGE CAPACITY			K_2O			MgO			Fe_2O_3			SiO_2/R_2O_3			ORGANIC MATTER		
			C	F	S	C	F	S	C	F	S	C	F	S	C	F	S	C	F	S
			m.e.	*m.e.*	*m.e.*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*				*per cent*	*per cent*	*per cent*
14042	IVd	1	47	62	64	2.40	1.70	1.34	2.36	2.46	2.62	15.05	18.63	14.32	2.80	2.55	2.90	....	....	.....
14039	IVa	1	48	69	88	2.15	1.56	0.96	2.24	2.22	1.89	10.56	12.12	11.39	3.23	2.85	2.97	....	....	2.85
14037	IIa	1	62	76	81	1.74	1.43	0.89	2.01	1.92	1.71	8.42	10.88	10.66	3.12	2.88	2.99	2.18	1.39	3.91
14034	Ia	1	42	64	..	2.17	1.93	0.76	1.55	1.79	1.29	6.38	9.42	7.99	3.52	2.96	3.03	7.18	3.65	23.22
14065	Ia	3	46	..	..	2.39	1.31	0.29	1.15	1.34	0.95	5.78	9.77	6.17	3.79	2.96	2.87	4.78	3.92	39.62
14083	Ia	5	31	..	47	1.74	1.28	0.44	0.81	1.02	0.59	5.56	8.32	4.25	4.13	2.86	2.53	4.82	....	36.10

* C, F, and S = coarse, fine, and superfine fractions, respectively.

TABLE 5

Variations in shale parent material with weathering

NUMBER	HORIZON	RELATIVE ORDER OF DEVELOPMENT	BASE EXCHANGE CAPACITY			K_2O			MgO			Fe_2O_3			SiO_2/R_2O_3			COLLOID			ORGANIC MATTER		
			C	F	S	C	F	S	C	F	S	C	F	S	C	F	S	C	F	S	C	F	S
			m.e.	*m.e.*	*m.e.*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*				*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
DS43	Shale	1	13	20	27	6.43	6.93	6.25	3.59	3.93	3.74	8.30	6.64	6.44	2.90	2.89	3.23	24	8.2	7.5	....	....	....
14700	IVb	2	21	33	46	6.00	5.78	5.07	3.30	3.62	3.19	8.38	10.73	8.92	3.17	2.83	3.20	23	7.4	7.0	0.96	1.02	4.20
14699	IIb	3	16	29	52	5.32	4.77	3.92	2.92	3.22	2.89	7.83	10.89	10.01	3.07	2.69	3.00	22	11.4	10.6	0.77	1.10	2.91

CHEMICAL VARIATIONS AMONG THE COARSE, FINE, AND SUPERFINE COLLOIDS IN THE HARTSBURG-CISNE DEVELOPMENTAL SERIES

The chemical variations among the size fractions are shown in table 4. The base-exchange capacity increases regularly with the decrease in particle size. There is good evidence that this is mainly due to a variation in the minerals which make up the colloids and accompany the size variations rather than to decreased particle size itself. The iron and water (not given in the table) increase with decreasing particle size. The K_2O decreases with particle size and advancing development while the MgO varies mainly with the latter. When free Fe_2O_3 is present it concentrates relatively more in the fine fraction.

CHANGES IN A SHALE COLLOID CAUSED BY WEATHERING

In Ford County, Illinois, occurs a shale material deposited in place by glacier action and relatively uncontaminated by other materials (11). The parent shale has been identified as Maquoketa shale. This material is partially weathered in the IVb or carbonate horizon and more weathered in the II horizon, which is now carbonate free. The developmental series in this case is represented by three steps, parent shale, IV horizon, and II horizon.

Table 5 gives the values obtained for the colloid fractions. Although the K_2O and MgO are generally higher and the base-exchange capacity is generally lower, the trend in values is of the same kind and order as that found in the loess soil colloids.

THE RELATION OF K_2O, MgO, $\frac{SiO_2}{R_2O_3}$ RATIO, AND BASE-EXCHANGE CAPACITY TO MINERAL NATURE AS BROUGHT OUT IN THE TWO DEVELOPMENTAL SERIES STUDIED

It has been shown that in both developmental series the trends are similar, but if we compare the Maquoketa shale developmental series with the Hartsburg-Cisne loess developmental series it is readily seen that the former represents a less developed series than the latter. The two series have, therefore, been combined, giving a series covering a wider range of development, and some of the superfine colloid values for this entire range are plotted in figure 2. A coarse colloid from a Cecil soil is included at the extreme right. The least developed colloid is plotted at the extreme left, and approximately similar degrees of development are plotted close together, although the order of relative development is maintained.

The curves in figure 2 express the differences already pointed out in the individual discussions of the data. They bring out, however, significant features not revealed by the former presentation of the data in tables 2, 3, 4, and 5. They show that K_2O decreases to a practically insignificant value at the same time that the base-exchange capacity and MgO become equal to each other. This occurs in the fifth colloid from the left. From there on the

MgO and base-exchange capacity remain practically equal to each other except in the later stages of advancing development where the MgO is somewhat lower than the base-exchange capacity and the $\frac{SiO_2}{R_2O_3}$ ratio also decreases.

At the point of maximum base-exchange capacity the colloids correspond to the empirical formula $Rep_2O \cdot MgO \cdot (Al_2O_3)_6(SiO_2)_{18}(H_2O)_{15}$ where Rep stands for replaceable cations and iron can partially replace aluminum. This is the formula previously published by the writer (2) as representing the principal clay mineral occurring in the Illinois loess soils. That changes are occurring with advancing development is shown by the decreasing MgO and Rep_2O values as well as the decreasing $\frac{SiO_2}{R_2O_3}$ ratios on the left hand side of figure 2.[5]

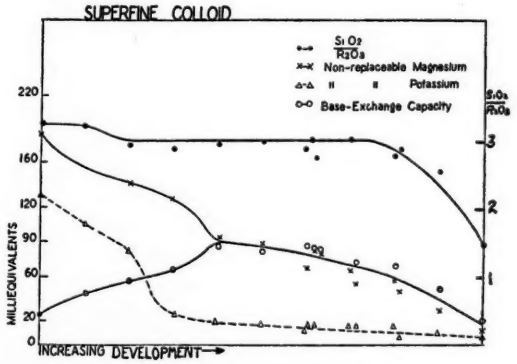

FIG. 2. THE DEVELOPMENT OF BASE-EXCHANGE CAPACITY IN THE SUPERFINE COLLOID

REFERENCES

(1) BRAY, R. H. 1934 A chemical study of soil development in the Peorian loess region of Illinois. *Amer. Soil Survey Assoc. Bul.* 15: 58–65.

(2) BRAY, R. H. 1935 The origin of horizons in claypan soils. *Amer. Soil Survey Assoc. Bul.* 16: 70–75.

(3) BRAY, R. H., GRIM, R. E., AND KERR, PAUL F. 1935 Application of clay mineral technique to Illinois clay and shale. *Bul. Geol. Soc. Amer.* 46: 1909–1926.

(4) BROWN, I. C., AND BYERS, H. G. 1932 The fractionation, composition and hypothetical constitution of certain colloids derived from the great soil groups. U. S. Dept. Agr. Tech. Bul. 319.

(5) GLINKA, K. D. 1927 The great soil groups of the world and their development. Mimeographed translation by C. F. Marbut, p. 35.

[5] The mineralogical significance of these changes has been worked out. Excellent proof that the shale mica (3, 6) is altering to the above base-exchange mineral without the accumulation of any intermediate products has been obtained. Various phases of this work will be presented in later papers.

(6) GRIM, R. E. 1935 Petrology of the Pennsylvanian shales and noncalcareous underclays associated with Illinois coals. *Jour. Amer. Ceramic Soc.* 14: 1–18.

(7) KELLEY, W. P. 1929 The determination of the base-exchange capacity of soils and a brief discussion of the underlying principles. *Jour. Amer. Soc. Agron.* 21: 1021–1029.

(8) MARBUT, C. F. Mimeographed lectures on soil genesis and classification. Lecture III, pp. 8–10.

(9) NORTON, E. A. 1933 The genesis and morphology of the prairie soil. *Amer. Soil Survey Assoc. Bul.* 14: 40–42. [See also J. S. JOFFE 1936 Pedology, pp. 234–235. Rutgers University Press, New Brunswick, N. J.]

(10) NORTON, E. A., AND SMITH, R. S. 1928 Horizon designation. *Amer. Soil Survey Assoc. Bul.* 9: 83–86.

(11) STAUFFER, R. S. 1935 Influence of parent material on soil character in a humid, temperate climate. *Jour. Amer. Soc. Agron.* 27: 885–894.

SOME EFFECTS OF CARBON DIOXIDE ON THE DECOMPOSITION OF ORGANIC MATTER AND THE ACCUMULATION OF NITRATES IN THE SOIL[1]

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Under normal soil conditions when no crop is growing upon the land, carbon dioxide is produced chiefly by microbiological action which brings about the decomposition of organic matter. In well-aerated soils the carbon dioxide produced does not accumulate to any great extent but diffuses through the soil and largely out into the atmosphere. The concentration of carbon dioxide in the soil air is usually below 1 per cent but may reach 1.5 to 2 per cent under certain conditions. The amount of carbon dioxide in the soil air under normal conditions, however, is probably never great.

The autotrophic bacteria obtain their carbon for energy and for building up their body substance from the carbon dioxide of the atmosphere or from that in solution, and there is some evidence that the heterotrophic organisms may also be stimulated to greater growth by the presence of carbon dioxide. Lundegardh (1) found the soil to be a more important source of carbon dioxide for growing plants than is the air. Investigations dealing with the addition of carbon dioxide to the soil for the benefit of crop plants have been reported, but the effects of these additions on the microbiological processes in the soil have not been studied in detail. The purpose of the work reported in this paper was to study the effect of additions of carbon dioxide to the soil on microbiological action as measured by the evolution of carbon dioxide and the production of nitrate nitrogen.

EXPERIMENTAL

Methods of procedure

The experiment as planned involved the addition of carbon dioxide to the soil as a gas and dissolved in water and it included a comparison of the results with those obtained in untreated soils and in soils aerated with a mixture of nitrogen and oxygen. The latter series was included in order to provide a test in which the air of the soils was kept relatively free of carbon dioxide, without aerating the soil excessively by drawing carbon dioxide-free air through it by aspiration.

[1] Journal Paper No. J383 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project No. 446.

The soil used was Carrington loam, with a pH of 6.33. It was passed through a quarter-inch screen and thoroughly mixed; 39 pounds was placed in each of 64 four-gallon earthenware pots. These were divided into four series of 16 pots each, and 4 pots in each series were treated as follows:

A. Check
B. 0.2 per cent oat straw
C. 0.2 per cent oat straw and 0.2 per cent rock phosphate
D. 0.2 per cent oat straw, 0.2 per cent rock phosphate, and 0.1 per cent limestone

In series 1 the soils received no further treatment and served as checks. Carbon dioxide-saturated water, referred to as "carbonic acid" and having a pH of 4.2, was added to the soils in series 2. In series 3 carbon dioxide gas was added to the soils from below at the rate of 5 liters per hour for 1 hour each day throughout the experiment. The soils in series 4 received a mixture of 1 part oxygen to 4 parts nitrogen gas, also added at the rate of 5 liters per hour for 1 hour each day throughout the experiment. The gases were regulated and measured by means of flow meters as shown in plate 1. The moisture content of the soils was adjusted to 20 per cent and maintained at this amount by frequent additions of distilled water, except in the case of series 2 where carbonic acid was used.

The soil in one pot of each treatment was kept fallow and was sampled at intervals for analysis. Three pots of soil in each treatment were used for the determination of the concentration of carbon dioxide in the soil air.

Concentration of carbon dioxide in the soil air

The concentration of carbon dioxide in the soil air was determined at the beginning of the experiment and at weekly intervals for 5 weeks. The Haldane gas analysis apparatus and a special soil tube (2) were used for this determination. The concentration of carbon dioxide in the soil air was determined just before the addition of carbon dioxide gas each day, except in one case, when the determination was made just after the addition of the gas. The results of the latter determination were as follows:

Per cent carbon dioxide in the soil air just after addition

CHECK	STRAW	STRAW + PHOSPHATE	STRAW + PHOSPHATE + LIME
38	50	50	55
40	40	40	74
45	40	48	35

The results obtained where the determinations were made in the beginning of the experiment and before the daily application of carbon dioxide are presented in table 1.

There was considerable variation in the concentration of carbon dioxide in

TABLE 1

Per cent of carbon dioxide in the soil air

TREATMENT	DATE OF SAMPLING	SERIES 1—CHECK			SERIES 2—CARBONIC ACID			SERIES 3—CARBON DIOXIDE GAS			SERIES 4—OXYGEN + NITROGEN		
		A	B	C	A	B	C	A	B	C	A	B	C
None	Nov. 13	0.62	0.70	0.96	0.20	0.30	0.40	8.30	7.60	4.90	0.30	0.40	0.30
	Nov. 20	0.40	0.30	0.80	0.60	0.40	0.60	4.80	5.60	3.20	0.30	0.50	0.30
	Nov. 27	0.10	0.40	0.40	0.70	0.30	0.30	0.50	0.30	0.50	0.40	0.10	0.10
	Dec. 4	0.10	0.10	0.40	0.10	0.30	0.20	0.80	0.10	0.20	0.05	0.10	0.10
	Dec. 18	1.00	0.37	0.30	0.20	0.10	0.10	1.50	0.10	0.40	0.20	0.05	0.50
Straw	Nov. 13	3.20	2.80	1.80	3.30	2.50	2.90	14.70	8.50	12.40	1.10	1.40	2.40
	Nov. 20	0.70	2.50	2.10	1.30	2.70	2.80	9.40	4.40	6.50	1.80	1.50	1.60
	Nov. 27	0.50	0.80	0.60	1.10	0.50	0.80	0.40	0.90	0.80	0.10	0.30	0.40
	Dec. 4	0.40	0.40	0.30	0.50	0.30	0.40	0.20	0.60	0.40	0.10	0.30	0.30
	Dec. 18	0.30	0.50	0.40	0.80	0.40	0.40	0.30	0.60	1.40	0.05	0.05	0.40
Straw + PO_4	Nov. 12	2.00	1.60	1.40	3.80	2.80	2.40	4.90	10.00	3.70	1.40	2.30	1.40
	Nov. 20	2.00	2.20	1.20	4.40	2.80	2.00	5.30	10.50	3.00	1.20	2.20	1.40
	Nov. 27	0.50	0.70	0.50	0.70	0.80	0.80	0.40	0.70	0.50	0.30	0.50	0.40
	Dec. 4	0.20	0.20	0.30	0.10	0.10	0.20	0.10	2.00	0.90	0.10	0.50	0.20
	Dec. 18	0.50	0.40	0.50	0.50	0.40	0.40	0.70	2.50	0.40	0.20	0.10	0.30
Straw + PO_4 + Lime	Nov. 12	3.80	2.70	1.70	3.20	1.40	1.50	6.80	10.30	8.20	1.80	3.30	2.80
	Nov. 20	4.00	3.00	2.60	4.20	3.20	1.50	5.50	9.50	6.40	1.40	2.40	2.80
	Nov. 27	0.60	0.70	0.70	1.10	0.60	1.10	0.80	0.70	0.60	0.30	0.40	0.50
	Dec. 4	0.20	0.20	0.30	0.30	0.20	0.50	0.80	0.50	0.50	0.20	0.20	0.20
	Dec. 18	0.40	0.30	0.50	0.70	0.50	0.70	2.20	5.40	1.10	0.20	0.20	0.20

TABLE 2

Analysis of variance of percentage of carbon dioxide in the soil air

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE
Between classes	79	1136.9215	14.3914
Between means of dates	4	429.9126	107.4782*
Between means of soil treatment	3	41.3834	13.7945*
Between means of series	3	276.2612	92.0871*
Interactions:			
Series x date	12	291.3647	24.2804*
Treatment x date	12	46.4368	3.8697*
Series x treatment	9	9.7102	1.0789
Treatment x series x date	36	41.8526	1.1626
Within (error)	160	150.2448	0.9390
Total	239	1286.9436	

* Highly significant.

the air in the soil in the different pots, but the data show at a glance that the addition of carbon dioxide gas in series 3 greatly increased the concentration of carbon dioxide of the soil air over that in the check soil and that aeration of the soil with a mixture of nitrogen and oxygen in series 4 decreased slightly the concentration of carbon dioxide in the atmosphere of these soils. Other differences are apparent, but an analysis of variance of the data given in table 2 shows the significance of these differences. This analysis shows a highly significant difference in the mean concentration of carbon dioxide at the different dates, between the different soil treatments, and between the different series. It is further shown that a highly significant difference in the concentration of carbon dioxide in the soil air was obtained by the addition of straw to the soil and that this difference was greatest where carbon dioxide was added either as the gas or in solution. The phosphate and lime in addition to the straw were without appreciable effect, except in two cases; namely, in series 1 and series 3 where the addition of lime increased the concentration of carbon dioxide of the soil air significantly over that of the soil treated with straw and phosphate. There was a highly significant difference in the concentration of carbon dioxide in all soils at the different dates of sampling during the first 3 weeks of the experiment, except where phosphate and phosphate and lime were added. In the latter cases the differences were not significant between the first and second samplings but were highly significant at the third sampling. The relatively small interaction (series x treatment) mean square indicates the same effect of treatment in the different series. In other words, the application of straw increased the concentration of carbon dioxide in the soil in all series.

The data show that the addition of carbon dioxide to the soil either in solution or as a gas increased significantly the concentration of carbon dioxide in the soil air during the first 3 weeks of the experiment. Three weeks after the beginning of the experiment the concentration of carbon dioxide decreased but was still higher in the soils treated with CO_2-gas than in the check soil.

Carbon dioxide production

The fallow soils of series 1 and 2 (check and carbonic acid) were sampled at monthly intervals beginning 1 month after the treatment of the soils in the greenhouse and continuing through December, January, February, and March for carbon dioxide production determinations in the laboratory. The moist soils were passed through the 2-mm. sieve, and the rate of carbon dioxide production was determined over a period of 9 days by the respiration chamber method (3). The average daily production of carbon dioxide in milligrams per 24 hours is shown in figures 1 to 4, and an analysis of variance of the data, in table 3.

The figures show that the addition of carbonic acid to the soil decreased the rate of carbon dioxide production in every case where straw was added to the soil and in every case, except at the February sampling, where no straw

was applied. There was never a great difference between the average rate of carbon dioxide production in the untreated soil watered with distilled water and that of soils watered with carbon dioxide-saturated water. However, there were significant differences where straw; straw and phosphate; or straw, phosphate, and lime were added. These differences in rate of carbon dioxide production in the check soils and in those of the carbonic acid series were

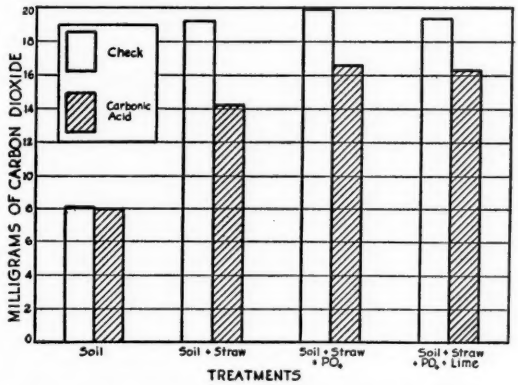

FIG. 1. RATE OF CARBON DIOXIDE EVOLUTION FROM SOILS—DECEMBER SAMPLING

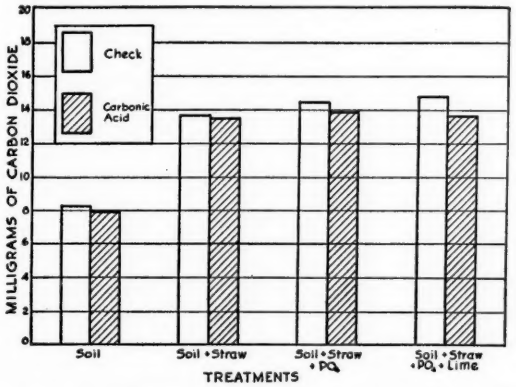

FIG. 2. RATE OF CARBON DIOXIDE EVOLUTION FROM SOILS—JANUARY SAMPLING

greatest at the first sampling, becoming somewhat smaller at the two succeeding samplings and increasing at the last sampling. The phosphate and lime additions stimulated the rate of carbon dioxide production in all cases, except at the February sampling, where the rate of carbon dioxide production was slightly less in the soil treated with straw and phosphate than in the soils treated with straw or those treated with straw, phosphate, and lime. This difference, however, was not significant.

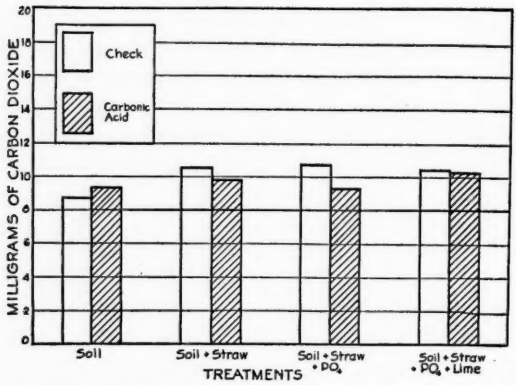

FIG. 3. RATE OF CARBON DIOXIDE EVOLUTION FROM SOILS—FEBRUARY SAMPLING

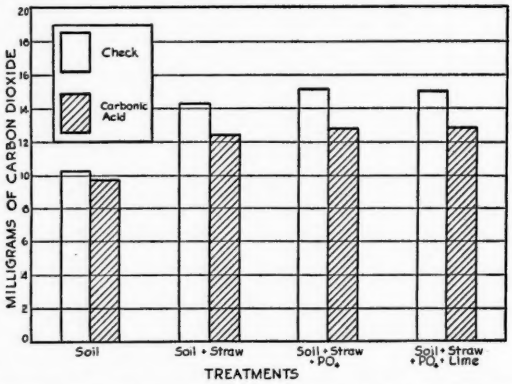

FIG. 4. RATE OF CARBON DIOXIDE EVOLUTION FROM SOILS—MARCH SAMPLING

TABLE 3

Analysis of variance of average daily production of carbon dioxide in soils

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE
Between means of treatments	3	355.4895	118.50*
Between means of series	1	40.8960	40.8960*
Between means of dates	3	223.6197	74.54*
Interactions:			
Date x series	3	9.9246	3.31
Date x treatment	9	91.9909	10.22
Series x treatment	3	15.5179	5.17
Series x treatment x date	9	11.4789	1.28
Within (error)	32	27.1056	0.85
Total	63	776.0231	

* Highly significant.

Nitrate production

The fallow soils in all series were sampled at the beginning of the experiment and at monthly intervals thereafter until April for the determination of nitrate content. The nitrate-nitrogen was determined by the phenoldisulfonic acid method. The results obtained are presented in tables 4 and 5.

TABLE 4

Effect of carbon dioxide on nitrate accumulation

TREATMENT	DATE OF SAMPLING	NO_3-N ACCUMULATION			
		Series 1—Check	Series 2—Carbonic acid	Series 3—CO_2 gas	Series 4—Oxygen + nitrogen
		p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*
Soils	Nov.	20.83	20.83	20.83	20.83
	Dec.	28.57	39.02	26.22	35.08
	Jan.	20.08	44.46	19.12	21.05
	Feb.	47.05	52.94	41.66	71.43
	Mar.	47.61	49.59	32.26	57.18
	April	28.16	34.38	28.22	48.78
	Av.	32.05	40.20	28.05	42.39
Soil + Straw	Nov.	20.83	20.83	20.83	20.83
	Dec.	0.0	0.0	0.0	0.0
	Jan.	4.35	12.50	8.32	13.82
	Feb.	13.11	32.51	16.91	23.09
	Mar.	30.55	36.36	22.72	39.29
	April	32.29	33.06	29.86	30.78
	Av.	16.85	22.54	16.44	21.30
Soil + Straw + PO_4	Nov.	20.83	20.83	20.83	20.83
	Dec.	0.0	0.0	0.0	0.0
	Jan.	9.19	12.32	8.55	12.38
	Feb.	18.08	10.92	16.03	16.91
	Mar.	27.86	13.88	27.58	33.61
	April	21.05	7.95	23.01	21.05
	Av.	16.17	10.98	16.00	17.46
Soil + Straw + PO_4 Lime	Nov.	20.83	20.83	20.83	20.83
	Dec.	11.44	15.03	0.0	13.33
	Jan.	9.52	17.61	11.55	19.48
	Feb.	24.09	23.68	20.77	33.47
	Mar.	37.73	32.26	28.17	49.19
	April	25.40	30.18	18.02	28.66
	Av.	21.50	23.26	16.56	27.49

The data in the tables show that there were highly significant differences in the nitrate content of the soils variously treated, that these differences varied at the different samplings, and that the differences in the nitrate content of the soils of the different series were significant but that the interaction, series x date, was not significant. In other words, the nitrate content of the soils of

the various series, regardless of other soil treatment, tended to vary in the same direction at the different samplings. Further analysis of the data shows that all soils in the series aerated with a mixture of nitrogen and oxygen contained a greater amount of nitrate-nitrogen than that of the check soil, and the difference was highly significant. The soil watered with carbonic acid also contained a significantly higher nitrate content than the check soil, but the soil to which carbon dioxide gas was added did not contain a significantly different amount of nitrate-nitrogen from that in the check soil.

The addition of straw to the soil decreased nitrate accumulation in all cases, but the decrease was less where phosphate and lime were also applied than where the straw was applied alone. The application of straw and phosphate depressed nitrate accumulation more than did the straw alone or the straw, phosphate, and lime.

TABLE 5

Analysis of variance of p.p.m. nitrate-nitrogen in soils

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE
Between means of series	3	6814.2982	2271.4327*
Between means of dates	4	6754.6380	1688.6595*
Between means of treatments	3	998.5558	332.8519*
Interactions:			
Series x date	12	1577.1149	131.4262*
Treatment x date	12	524.4357	43.7030
Series x treatment	9	812.3762	90.2640
Treatment x date x series (experimental error)	36	798.7321	22.1870

* Highly significant.

The average nitrate content of all soils increased significantly from December to March, and the nitrate content at the April sampling was significantly lower than at the March sampling, but the highly significant interaction, treatment x date, indicates that the nitrate content of the variously treated soils did not follow this trend. An examination of the data shows that the nitrate accumulation in the untreated soil reached a peak in February, whereas the peak in all of the other soils was not attained until March.

DISCUSSION AND SUMMARY

The carbon dioxide added to these soils as a gas diffused through the soil into the atmosphere rather rapidly, but there was sufficient accumulation to maintain a considerably higher concentration in the soil air than was present in the soils of the other series. There was also a higher concentration of carbon dioxide in the soils treated with carbonic acid than in the check soils. Presumably, the soil solution of series 2 contained a higher concentration of carbon dioxide than that of the other soils.

The accumulation of carbon dioxide in the soil depressed the initial rate of decomposition of organic matter in the soils to which straw was added. This depressing effect was evident 4 months after the straw was added. The depressing effect of carbon dioxide on the rate of decomposition of organic matter was not so pronounced in the untreated soils as in the soils treated with straw. Presumably there were fewer and less active organisms and species differences in the untreated soils than in the straw-treated soils and the depressing effect of the carbon dioxide in the straw-treated soils resulted from an oxygen deficiency at a time when optimum aeration was required for rapid decomposition.

The treatment with carbonic acid was effective in stimulating nitrate production, but the treatment with carbon dioxide gas was without significant effect. The stimulation of nitrate production by the carbonic acid was undoubtedly related to the increased solubility of the mineral constituents required by the nitrifying organisms. The failure of carbon dioxide gas to affect the nitrate content of this soil indicates that carbon dioxide was not a limiting factor in nitrification. The stimulation of nitrification by aeration with nitrogen and oxygen indicates that perhaps the concentrations of carbon dioxide attained in the soils of series 3 were sufficiently high to create an oxygen deficiency.

REFERENCES

(1) LUNDEGARDH, H. 1925 Klima and Boden. Fischer, Jena.

(2) SMITH, F. B., AND BROWN, P. E. 1931 The concentration of carbon dioxide in the soil air under various crops and in fallow soils. *Iowa State Col. Jour. Sci.* 8: 1–16.

(3) SMITH, F. B., BROWN, P. E., AND MILLAR, H. C. 1935 The rhythmical nature of microbiological activity in soil as indicated by the evolution of carbon dioxide. *Jour. Amer. Soc. Agron.* 27: 104–108.

PLATE 1

APPARATUS FOR APPLYING CARBON DIOXIDE TO SOILS

ACCURACY OF A SOIL THERMOGRAPH

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Biological studies in connection with organisms inhabiting the soil frequently involve the amassing of data dealing with soil temperatures. These data are obtained by various methods, mercury thermometers, thermocouples, and frequently by soil thermographs. One of the most widely used thermographs is known as a "soil or distance thermograph." This instrument consists essentially of a buried sensitive bulb connected to the instrument head, the recording part of the system, by a flexible capillary tube protected by a 4-ply copper braiding. The bulb itself is 12 inches long by $1\frac{1}{16}$ inches in diameter.

The question has been raised as to the validity of the results obtained by this instrument in the case of temperature measurements at very shallow depths, since the bulb is bulky and, at depths of 1 or 2 inches, is exposed to a sharper temperature gradient than would be experienced at greater depths. Furthermore, the braided copper covering of the capillary is itself an excellent conductor, and if the copper bulb were buried at shallow depths almost all of the 10 feet of capillary tubing would be exposed in a temperature varying greatly from that of the bulb. Would this exposure affect the readings of the bulb to any extent? The makers claim that "correct compensation is made for temperature effects on the instrument head," and this is an important consideration. In an effort to check up on some of the points brought out, one of these instruments was subjected to very extreme conditions, more extreme than would ever be likely to occur in nature. The results obtained are presented herewith.

PROCEDURE

A stout wooden box was filled with sifted loam soil to a depth of 7 inches. Coiled in the bottom of the box was a tube through which cold water was circulated continuously. The bulb of the thermograph was buried with its long axis exactly 2 inches below the surface. About $\frac{1}{8}$ of an inch from the bulb was erected a set of thermocouple points running vertically from the soil surface to the bottom of the box, the points being 1 inch apart except at the 1-inch to 3-inch depth, where they were $\frac{1}{8}$ of an inch apart. With one thermocouple above the soil surface this made couple No. 9 (reading from the top) exactly opposite the median axis of the bulb (fig. 1). The box and its contents were placed in a cabinet the air of which was heated with resistance heating elements,

and this portion of the set-up was not disturbed throughout the duration of the experiment. There was thus set up a sharp temperature gradient in this 7 inches of soil, which was sufficiently stable to enable tests to be made of the efficiency of the thermograph. The system was allowed to come to equilibrium before readings were made. The thermograph indicator was carefully checked and set to agree with the thermocouple readings before the experiment was started.

RESULTS

After running for some hours the bulb and the thermocouple both registered the same temperature. This agreement was maintained throughout the continuance of the conditions described.

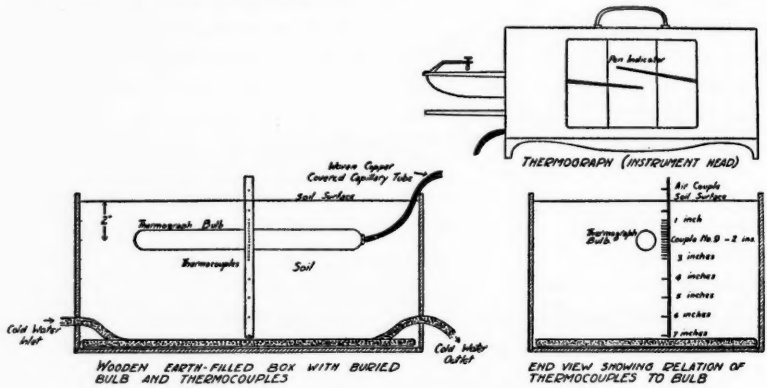

FIG. 1. DIAGRAM SHOWING THE SET-UP USED TO TEST THE ACCURACY OF A SOIL THERMOGRAPH

The temperature in the cabinet was raised until the thermograph needle registered its upper limit. After one of the heating units was removed the temperature in the box dropped slowly. Readings taken during this time showed that the bulb was not so sensitive to quick changes as was the thermocouple. On a rising temperature the bulb tended to lag behind the thermocouple, and on a falling temperature there was also a lag on the part of the bulb.

All the readings shown in table 1 were made with the thermograph and most of the cable at room temperature (75°F.) Most of the cable was now placed in the heated cabinet, and the thermograph was set on the hot glass top of the cabinet. After 2 hours it was observed that the buried bulb was starting to act as a heating element by reason of the heat conducted down the copper cable. The bulb was then approximately 2° higher than the thermocouples. This difference continued during the day. On the final reading for this set-up the system had become stable. The thermograph had levelled out at 109.7,

still 2.5° warmer than the thermocouple, apparently because of the heat transferred to the bulb by the cable. Overnight the discrepancy increased somewhat, and the thermograph record showed that the recorded temperature had been maintained without fluctuation for several hours. The readings at the end of the day and the first reading next morning are as follows:

Thermocouple No. 9	*Thermograph*	*Discrepancy*	*Temperature inside Instrument head*	*Temperature of copper tube inside cabinet*
107.2	109.7	2.5	111.2	192.2
106.2	110.0	3.8	107.6	194.9

The set-up was again changed. The thermograph and all but 2 feet of the copper cable were placed in a refrigerator. The 2 feet of exposed cable was partly at room temperature and partly within the heated cabinet. After an hour the first reading was made and showed at this time that the thermo-

TABLE 1

Readings during rising and falling temperatures

	COUPLE NO. 9	THERMOGRAPH	LAG
	°F.	°F.	°F.
Falling:			
8 a.m.	107.4	110.0	2.6
9 a.m.	102.2	105.2	3.0
10 a.m.	98.2	102.0	3.8
11 a.m.	96.8	101.0	4.2
12 noon	99.5	100.3	0.8
Rising:			
1 p.m.	101.1	101.1	0
2:30 p.m.	102.7	102.5	0.2
3 p.m.	103.6	103.0	0.6
3:30 p.m.	104.0	103.2	0.8
8:45 p.m.	106.8	105.8	1.0

couple and thermograph were in agreement. Subsequent readings showed decidedly the effect of the cooling influence of the refrigerator on the instruments, a difference that became more marked with longer exposure to the cold in spite of the fact that the temperature of the ice box was slowly rising. The observed differences are as follows:

Time	*Thermocouple No. 9*	*Thermograph Pen Indication*	*Difference*	*Temperature inside Instrument head*
11 a.m.	107.1	107.1	0	53.2
1 p.m.	106.2	104.0	2.2	31.1
2 p.m.	107.6	103.8	3.8	31.5
3 p.m.	107.6	103.8	3.8	33.5
4 p.m.	107.1	103.0	4.1	35.1
9 p.m.	105.8	102.8	3.0	50.0

Following this experiment the system was restored to conditions of the original experiment, when after several hours the thermocouple and thermo-

graph readings were once more in agreement. The system was then dismantled and the thermograph again checked against the couples, when both were found to agree closely.

CONCLUSIONS

That the conditions described are most extreme and not likely to be encountered under normal conditions is granted; yet it is indicated that under certain circumstances the readings of a thermograph may not be exact.

In the Centennial Valley in Montana, at 7000 feet altitude, one of these thermographs records winter soil temperatures at 2 inches. Although the air temperatures drop to very low points, at times to −60°F. during the coldest part of the day, there is a snow blanket beneath which the soil surface temperatures will rarely go much below zero. With the bulb buried at so shallow a depth, most of the capillary cable is in the air, and, with the instrument head exposed to −60°F. we have, therefore, in this instance an actual case where there is a 60° difference between the instrument and the bulb, and the record may be off as much as 3° from the actual temperature.

The temperature gradient in some soils, especially within the surface 4 inches, is often very sharp. With a thermograph bulb $1\frac{1}{16}$ inches in diameter buried with its median axis only 2 inches below the soil surface, as it is in grasshopper investigations, the combination of a sharp temperature gradient of some degrees within that space of $1\frac{1}{16}$ inches together with the conduction down the metal cable will result in error. For temperature measurements at greater depths this device ought to be very reliable.

RECOMMENDATIONS

To overcome the aforementioned difficulty it is suggested that for temperature measurements of shallow depths, at least 3 feet of the capillary tubing be buried at the same depth as the bulb, so that the tube will have an opportunity to come to equilibrium with the surrounding temperature before it connects with the bulb.

A RAPID METHOD FOR DETERMINING SOIL MOISTURE[1]

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University of Kentucky

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ADAPTABILITY

The method described in this paper is valuable for the quick determination of the percentage of moisture in soil. It is especially advantageous when many determinations are to be made upon one kind of soil. When a set of factors or a graph for the soil under investigation has been prepared carefully, determinations are accurate to about 5 parts per 1000, or to about 0.5 per cent.

The determinations may be made rapidly in the field with nothing but a thermometer, test tubes, a 2-cc. pipette, and concentrated sulfuric acid. Some provision must be made to weigh 1 gm. of soil rapidly. Spreading out samples to air dry to a constant weight is eliminated. If it is desired to determine moisture on the usual oven-dry basis, a few initial oven dryings may be made, to establish a curve, and then future oven drying is unnecessary when working with soil types which do not vary too much as to percentage of silica, organic matter, and basic constituents.

PRINCIPLES

The method is based on the fact that when water is added to concentrated sulfuric acid, a definite amount of heat is produced, proportional, within certain limits, to the quantities of water and acid mixed. With a fixed quantity of acid, the rise in temperature of the mixture will be definitely related to the quantity of water added and may serve as a measure of that quantity. Because the specific heat of water is greater than that of sulfuric acid, the rise in temperature when different quantities of water are added to a fixed quantity of acid is not exactly proportional to the quantity added, but diminishes somewhat as the quantity of water is increased. Thus a series of such temperature readings, with fixed quantity of acid and increased quantities of water could be plotted into a curve which would tend to flatten out as the quantity of water was increased.

Obviously, the free water in a soil should produce its proper amount of heat, when brought into contact with concentrated sulfuric acid. Experiment showed that when 2 cc. of concentrated sulfuric acid acted on 1-gm. portions of soil of different moisture content, a temperature curve was obtained very

[1] The investigation reported in this paper is in connection with a project of the Kentucky Agricultural Experiment Station and is published by permission of the director.

similar to that obtained with acid and water only. In the presence of soil, however, heat may be produced by the action of the acid on other substances than water. Besides, some heat is lost during the experiment, and some goes to raise the temperature of the solution and the apparatus. It is necessary, therefore, to prepare, under standardized conditions, a set of factors or reference curve for each different type of soil to be studied. This may be done by adding a measured quantity of acid to a weighed portion of soil and to other weighed portions to which accurately measured quantities of water have been added, and observing the maximum temperature each time.

TABLE 1

Temperature increases, in degrees centigrade, caused by varying increments of water added to a brown silt loam

Water additions in parts per thousand of the mixture

	WATER ADDED								
	0	20	100	150	200	250	300	350	400
Series 1	3.9	12.5	19.0	23.4	30.5	33.8	39.0	43.4	47.5
Series 2	3.7	11.7	19.5	24.1	31.5	34.0	39.5	43.5	47.5
Series 3	4.0	12.0	19.8	23.8	31.0	34.0	39.4	43.7	47.7
Series 4	4.0	12.5	18.5	23.2	32.0	34.0	....	43.0	47.8
Average	3.9	12.2	19.2	23.6	31.3	34.0	39.3	43.4	47.6

TABLE 2

Temperature increase, in degrees centigrade, caused by known additions of water to 1 gm. of soil of different types

H_2O ADDED	SANDY SOIL	BLACK SILT LOAM	CLAY SOIL
Dried at 100°C.	5.5	8.1	7.0
Air dry	5.9	13.5	11.0
50 mgm.	13.5	18.0	16.5
100 mgm.	20.8	23.5	22.8
150 mgm.	27.7	28.8	29.8
200 mgm.	32.5	33.0	36.3
250 mgm.	35.5	37.3	41.8
300 mgm.	38.8	42.3	46.3
350 mgm.	42.3	49.1	51.0
400 mgm.	45.8	53.5	55.0

TEMPERATURE-MOISTURE CURVE FOR A BROWN SILT LOAM

Tables 1 and 2 present results showing temperature increases obtained by adding known increments of water to the air-dry soil. The soil was air dried under normal conditions (20°C. and approximately 70 per cent relative humidity.) The moisture remaining in the soil was taken as approximating the water unavailable for plant use. Briggs and Shantz[2] have shown that the

[2] Briggs, L. J., and Shantz, H. L. 1912 The wilting coefficient for different plants and its indirect determination. *U. S. Dept. Agr. Bur. Plant Indus. Bul.* 230: 22.

moisture unavailable for plant use is approximately 1.47 times the hygroscopic coefficient, but it is most convenient and probably about as accurate to consider the moisture in the air-dry soil as that which is not available to plants. The temperature increases due to moisture above the air-dry soil must be calculated as shown in the last section of this paper.

PROCEDURE

One gram of air-dry soil was placed in the bottom of an ordinary dry 25-cc. test tube. Two cubic centimeters of 95 per cent C.P. sulfuric acid (Baker analyzed sp. gr. 1.835–1.840) was added. The soil and acid were mixed by stirring with a centigrade thermometer. The mixture was stirred vigorously and thoroughly for a few seconds. Then the rise in temperature was noted during only occasional and less vigorous stirring. The mercury rises very rapidly at first. Further stirring may make it rise farther as long as complete mixing has not been effected, but after complete mixing has been attained, stirring tends to cool the solution. Careful attention to observe the maximum

TABLE 3

Comparison of the gravimetric and thermometric methods in soil of three types

Moisture in parts per thousand of moist soil above that in the air-dry soil

SAMPLE NUMBER	BROWN SILT LOAM		BLACK SILT LOAM		SANDY SOIL	
	Gravimetric	Thermometric	Gravimetric	Thermometric	Gravimetric	Thermometric
1	104	104	135	135	54	57
2	132	136	152	162	55	48
3	137	124	164	170	62	55
4	140	130	168	162	63	62
5	146	147	169	170	64	68
6	147	140	170	167	75	75
7	152	149	170	170	78	82
8	155	158	176	175	81	75
9	158	157	179	160		
10	163	155				
11	166	165				

TABLE 4

Illustration of factor method of calculating soil moisture from temperature increases

PLOT	TEMPERATURE RISE	SOIL MOISTURE BY GRAVIMETRIC METHOD	FACTOR	SOIL MOISTURE BY THERMOMETRIC METHOD
	°C.	*p.p.t.*		*p.p.t.*
1	34.1	195	5.719	193.1
2	31.4	182	5.796	177.8
3	32.5	180	5.538	184.0
4	31.7	179	5.647	179.4
5	26.8	150	5.597	151.7
6	25.1	127	5.060	.....

temperature is necessary. A dry pipette must be used to measure the sulfuric acid. The difference between an accurate reading of the temperature reached and that of the original sulfuric acid is taken as the increase caused by moisture. With air-dry soil, the increase in temperature is due to moisture in the soil and to reactions between the soil and acid. Of course, the temperature of the soil should be approximately room temperature and about the same as that of the acid. In table 1 the temperature increase due to 0 water is the increase observed when 2 cc. of sulfuric acid was added to 1 gm. of air-dry soil, as directed above, whereas that for 50 parts per 1000 of water is the increase observed with 0.05 cc. and 0.95 gm. soil; that for 100 p.p.t. is the increase observed with 0.1 cc. of water and .90 gm. soil; etc.

METHOD OF STATING RESULTS

Percentage of moisture in the soil is usually stated as percentage of oven-dried soil (100°C.) in order to have a constant base. This, however, does not take into consideration the availability of water to plants. A peat soil may contain 50 per cent moisture and have no more available water than a silt loam with 20 per cent moisture. If the moisture is stated as parts per thousand in the moist soil above that contained in the air-dry soil, we then take into account the water available to plants and leave out most of that unavailable. Of course, the percentage of water in an air-dry soil is dependent on the temperature and relative humidity at the time of air drying, but usually this variation is small and does not warrant the time required to obtain standard conditions for drying. In tables 3 and 4 the moisture is expressed in parts per thousand of moist soil above that contained in the air-dry soil.

RESULTS

Variations in temperature readings on a uniform soil sample. Table 1 shows that the temperature increases due to additions of equal amounts of water to a uniform air-dry soil were very consistent and progressed in almost direct proportion to the increase in water added.

Differences between soil types. Table 2 shows that the temperature increases differ somewhat with different soil types. The nature of the reactive compounds and the differences in specific heats of soil compounds undoubtedly are largely responsible for these fluctuations. These results show that definite curves have to be determined for each soil type.

Variations due to loss of heat. Radiation will vary with temperature and air movement and the effect on temperature rise will be appreciable. Precautions must be taken to keep temperature and air movement as nearly as possible the same as when the reference curve was made. Variations of a few degrees will not make noticeable differences, but temperature variations of over 5°C. are likely to cause significant differences. The temperature at which each reference curve was made should be specified. The temperature at which the determinations were made in this paper did not vary more than a few degrees from 25°C.

Comparison of methods. Table 3 gives the results of the temperature method compared with the weight method of determining soil moisture. Only 10 cases out of 28 differed over 5 p.p.t. and only 2 of these were over 10 p.p.t. This variation probably was largely because the temperature curve of the soil type was not quite accurate. If enough cases are used to give an accurate curve for a specific soil type it seems that the temperature method would be even more accurate than the weight method in the average technique used in routine work, since to get accurate results with the weight method good technique must be used in all weighings to prevent both moisture loss and moisture

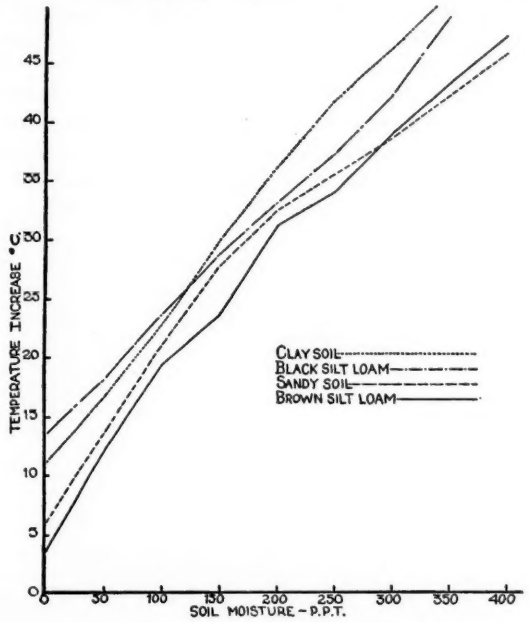

FIG. 1. INCREASES IN TEMPERATURE OBSERVED CORRESPONDING TO STATED ADDITIONS OF WATER TO 1 GM. OF SOIL AND 2 CC. OF SULFURIC ACID

uptake. This special technique can be used to establish the curve, and then rapid determinations by the temperature method may be made in the routine work, by assistants, with less danger of error from neglect or improper technique.

Table 4 presents the factors showing the relationship of moisture by the weight method to temperature increases. It will be noted that between 150 and 200 p.p.t. the factor is practically constant. The average factor is equal to the sum of the number of parts per thousand divided by the sum of the temperature increases. This equals $886 \div 156.5 = 5.661$. It will be seen that when this factor is used to calculate the parts per thousand the results

agree very closely with those found by the weight method. The factor begins to get smaller at 127 p.p.t., and if more determinations were made between 100 and 150 p.p.t. it probably would be lower than 5.66 and consequently a lower factor should be used in this range. Since the gravimetric determinations were referred to the air-dry soil this way of calculating moisture avoids any necessity of correcting for hygroscopic moisture and gives the results in parts per million on the air-dry basis.

The parts per thousand of moisture may also be calculated from curves as shown in figure 1. The data to construct these curves are best derived as in tables 1 and 2 by adding known increments of water to the air-dry soil, although if enough determinations by the weight method are made when the temperature increases are noted these may be used to plot the curves. If known increments of water are added, the temperature increase obtained is for total water and the temperature increase due to water above hydroscopic water will be the total temperature increase minus the increase for air-dry soil which has been multiplied by the amount of air-dry soil used. For instance, the temperature increase due to 50 p.p.t. added to air-dry brown silt loam is equal to $12.2-(3.9 \times .95)$.

APPARATUS FOR THE MEASUREMENT OF SHRINKAGE COEFFICIENT OF SOILS

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Determinations of friability, shrinkage coefficient, and relative moisture capacity of soils are of considerable agronomic significance. Not only do they provide an estimate of the power necessary to pull a tillage implement and a measure of the rate of moisture and plant root penetration but they also give an indication of the capacity of the soil for water retention and of whether the soil is likely to crack during the summer.

Haines (4) used a constant-volume bottle for determining the volume changes associated with variations in water content of soils. The technique consisted in weighing the mercury required to fill the bottle with and without a soil prism and calculating the volume of the displaced mercury. Puri, et al. (6) have recently described an apparatus for measuring the shrinkage of moist soils on drying. Although the instrument is fairly sensitive, only small volumes of soils within a narrow total range can be used for shrinkage determinations. Jennings and Peterson (5) adopted a modification of the method used by Christensen (1) for friability and shrinkage measurements. With a steel mold, the soil paste was made into cylinders 3.37 cm. long and 2.7 cm. in diameter. Shrinkage coefficients were determined by measuring the length and diameter of the cylinders in the beginning and at the end of the drying period. Evidently the molding of cylinders consumes a considerable time, and the cylindrical shape of the soil paste is likely to crack on drying unless great care is exercised in the operation.

In the course of investigations on the friability and shrinkage coefficients of certain soil types at Benares, a simple apparatus for the determination of soil shrinkage was developed in this laboratory and is described briefly in this paper. The principle of the apparatus consists in finding the volume of the gas space in a soil chamber with and without a soil ball and determining the volume of the soil ball by subtracting the one from the other. The volume of the gas space in the soil chamber is determined in the following manner: A portion of gas is withdrawn from the soil chamber, and its volume is determined at the atmospheric pressure; the lowering of pressure in the soil chamber following the withdrawal of the gas is also noted. By applying the Boyle-Mariotte law, the volume of the gas space in the soil chamber is easily computed from these data.

DESCRIPTION OF THE APPARATUS

The apparatus (fig. 1) consists of a 200-ml. soil chamber (*S*) which is similar to the one employed by Singh and Mathur (7) for the determination of CO_2 evolutions from soils and is provided with a ground glass stopper (*G*). The soil chamber (*S*) is connected through the glass stopper (*G*) with a 4-ml. measuring pipette (*P*) graduated into hundredths of a ml. To obviate error in the readings of (*P*) due to variations in the atmospheric temperature a com-

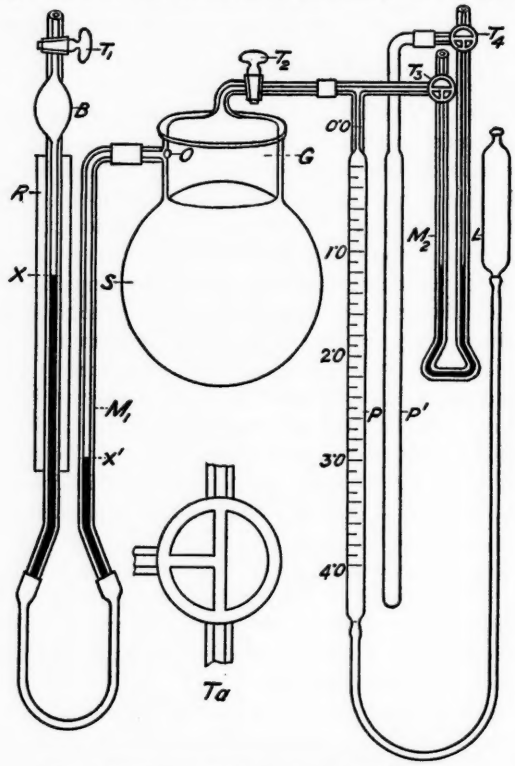

FIG. 1. APPARATUS FOR MEASURING SOIL SHRINKAGE

pensation pipette (*P'*) is provided. The gas within the measuring pipette (*P*) is maintained at the initial atmospheric pressure with the help of the manometer (M_2). Attached to the soil chamber (*S*) is a side tube with which is connected a manometer (M_1), based on the principle of Dickens-Greville constant-volume differential manometer (3). The two limbs of the manometer (M_1) are connected by a length of rubber tube, and the left-hand limb is secured by means of a spring clip and can be slid up or down. A strip of squared paper (*R*) is placed behind the left-hand limb, and each manometeric limb

carries a circular mark (X, X'). The bulb (B) serves to compensate for variations in the temperature of the soil chamber. The volume of the bulb (B) need not be equal to that of the soil chamber (S), since the increase of pressure produced by warming an enclosed volume of gas is the same whatever the volume of the containing vessel. By rotating the ground glass stopper (G), which carries an orifice (O), the communication between the soil chamber (S) and the manometer (M_1) is easily cut off or re-established.

MANIPULATION

Details of manipulation are as follows: The taps (T_1) and (T_2) are opened and the taps (T_3) and (T_4) turned in the position shown at (Ta). The soil chamber (S) is rotated on its ground glas stopper until a communication is established between (M_1) and (S) through the orifice (O). The left-hand limb of the manometer (M_1) is moved down until the marks (X) and (X') are on the same level when the manometeric liquid (Brodie solution[1]) should stand at these marks. The mercury in the pipette (P) is now adjusted to the "zero" mark. Since the pressure within the pipettes (P) and (P') is the same, i.e., equal to the atmospheric pressure, the Brodie solution in the manometer (M_2) should stand at the same level in both the limbs. Subsequent to this, all the taps (T_1), (T_2), (T_3), and (T_4) are closed. By lowering the levelling bulb (L), some gas from the soil chamber (S) is withdrawn into the pipette (P) and the tap (T_2) is closed. The left-hand limb of the manometer (M_1) is moved up until the manometric liquid again stands at the marks (X) and (X'). The vertical distance between the two meniscuses of the manometric liquid, representing the lowering of pressure within the soil chamber, is read on the squared paper, and the volume of the gas withdrawn into the pipette (P) is recorded after the manometer (M_2) is set. Now the soil ball is transferred to the soil chamber (S), and again the lowering of pressure in (S) following the withdrawal of an equal volume of gas into (P) is noted. The volume of the soil ball, say x, is given by the following formula:

$$x = v.\, H\left(\frac{1}{h_1} - \frac{1}{h_2}\right),$$

where v = volume of gas withdrawn into the measuring pipette;
H = initial atmospheric pressure in millimeters of Brodie solution;
h_1 = lowering of pressure in the soil chamber without the soil ball;
and h_2 = lowering of pressure in the soil chamber with the soil ball.

After the readings of the manometer (M_1) and the pipette (P) have been recorded, the tap (T_2) is opened, the mercury in the measuring pipette is adjusted so that the liquid levels in the manometer (M_2) are set once more, and the reading of the pipette (P) is recorded. Under these circumstances the mercury in (P) should stand at the zero mark; any appreciable change indi-

[1] The composition of the Brodie solution is as follows: 500 ml. water, 23 gm. NaCl, 5 gm. sodium tauroglycocholate, and a few drops of an alcoholic solution of thymol.

cates a leakage of gas during the procedure, in which case the whole process is repeated.

The range of the apparatus is varied easily to suit individual requirements by introducing a quantity of pure mercury into the soil chamber. The vertical distance between the meniscuses of the manometric liquid in the two limbs of the manometer (M_1) will be inversely proportional to the volume of the gas space in the soil chamber, provided equal volumes of gas are withdrawn from the latter in each case. Evidently the sensitivity of the apparatus can be increased by additions of weighed quantities of mercury to the soil chamber. In fact, it was found in practice that a layer of mercury if permanently left in the soil chamber facilitates considerably the introduction of the soil ball by acting as a sort of pad on which the soil ball floats.

TABLE 1

Shrinkage coefficients and relative moisture capacities of 40 soils belonging to five textural groups from the neighborhood of Benares

CLAY		CLAY LOAM		SILTY CLAY LOAM		FINE SANDY LOAM		SANDY LOAM	
Shrinkage coefficient	Relative moisture capacity	Shrinkage coefficient	Relative moisture capacity	Shrinkage coefficient	Relative moisture capacity	Shrinkage coefficient	Relative moisture capacity	Shrinkage coefficient	Relative moisture capacity
27.29	40.21	23.29	33.36	18.29	24.38	9.27	20.29	7.29	15.29
28.23	41.23	26.26	32.16	17.76	25.29	9.39	19.37	6.99	13.65
30.06	39.99	25.59	30.37	18.29	23.27	8.67	17.29	7.23	14.96
29.32	36.29	27.23	31.38	19.23	25.69	10.56	18.65	6.98	14.29
32.79	38.26	25.29	29.29	16.67	23.29	9.21	20.62	8.29	13.96
30.94	40.37	24.36	28.36	17.38	23.67	9.39	21.37	7.65	12.99
31.67	41.69	27.39	29.27	19.35	24.29	8.37	19.68	7.55	12.62
29.98	42.29	26.29	30.36	19.62	25.67	8.99	18.99	6.98	11.98

EXPERIMENTAL

Numerous soil samples were collected from the neighboring tracts and were labelled on the basis of a mechanical analysis (2) as clay, clay loam, silty clay loam, fine sandy loam, and sandy loam. Eight soils from each textural group were used for the determination of shrinkage coefficients and relative moisture capacities.

A quantity (60–80 gm.) of air-dry soil is placed in a porcelain dish, and a fine spray of water is made to play upon it as it is continuously agitated by means of a glass rod. Addition of water is continued until the soil is just wet enough to be handled without sticking to the hands, when it is transferred to a thick glass plate and thoroughly mixed with a long-bladed knife until the soil paste reaches a uniform moisture content. The soil paste is then made into a ball of a size that can be conveniently introduced into the soil chamber. A spheroidal shape of the soil paste is preferable, for not only is this shape convenient to handle but it shows the least tendency to crack on drying. The soil ball is left for some time in the air so that it dries slightly, it is then weighed, and its

volume is determined by means of the apparatus. Final drying of the ball is carried out by placing it for one day in an oven at a temperature of 110°C. At the end of the drying period it is removed from the oven, cooled in a desiccator, weighed, and its volume determined. Shrinkage coefficient and relative moisture capacity are calculated as follows:

$$\text{Shrinkage coefficient} = \frac{\text{volume of wet soil ball} - \text{volume of dry soil ball}}{\text{volume of wet soil ball}} \times 100$$

$$\text{and relative moisture capacity} = \frac{\text{weight of wet soil ball} - \text{weight of dry soil ball}}{\text{weight of dry soil ball}} \times 100.$$

The shrinkage coefficients and the relative moisture capacities of 40 soils belonging to the five textural groups examined are presented in table 1. The data indicate appreciable variations in the physical properties of different soils belonging to the same textural group. Clayey soils have a high shrinkage coefficient and a high relative moisture capacity, whereas the sandy ones possess a low relative moisture capacity and a low shrinkage coefficient. A high shrinkage coefficient indicates the preponderance of clay properties, i.e., a considerable resistance to the movement of the plow, a very slow rate of moisture and plant root penetration, and a high water-retaining capacity. Light soils, on the other hand, possess low values of shrinkage coefficient and are characterized by an easy penetrability to water and plant roots and a low capacity for water retention.

SUMMARY

A simple instrument for the measurement of the shrinkage coefficient of soils is described.

A few data with regard to the shrinkage coefficients and the relative moisture capacities of a number of soils belonging to five textural groups from the neighborhood of Benares are presented.

REFERENCES

(1) CHRISTENSEN, O. 1930 An index of friability of soils. *Soil Sci.* 29: 119–135.

(2) DAVIS, R. O. E., AND BENNETT, H. H. 1927 Grouping of soils on the basis of mechanical analysis. U. S. Dept. Agr. Cir. 419.

(3) DICKENS, F., AND GREVILLE, G. D. 1933 A constant-volume differential manometer. *Biochem. Jour.* 27: 213–219.

(4) HAINS, W. B. 1923 The volume-change associated with variations of water content in soils. *Jour. Agr. Sci.* 13: 296–310.

(5) JENNINGS, D. S., AND PETERSON, J. D. 1935 Drainage and irrigation, soil, economic and social conditions, Delta Area, Utah. Division 2. Soil conditions. Utah Agr. Exp. Sta. Bul. 256.

(6) PURI, A. N., TAYLOR, E. M., AND ASGHAR, A. G. 1934 A new apparatus for measuring soil shrinkage. *Soil Sci.* 37: 56–63.

(7) SINGH, B. N., AND MATHUR, P. B. 1936 Apparatus for the measurement of CO_2 evolved during the decomposition of organic matter in soils. *Jour. Amer. Soc. Agron.* 28: 423–426.

ON THE FORMATION OF STRUCTURE IN SOIL: III. MECHANISM OF THE SWELLING OF SOIL

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The structural element of soil may be regarded as a non-homogeneous system of particles of varying size. The order of the grouping of the individual elements of structure and the tenacity of the bond are determined by the structure of the fine elements. If we imagine a system, consisting of separated particles of colloidal size and of larger mineral elements, mixed with water, then after drying, the particles will retain on their surface a stable water film, which becomes common to all the particles collected together and kept near one another by the tension of this film (1, 2). These conceptions must be supplemented by an essential condition, namely, that the surface water film creates a definite orientation of the adjacent particles, which determines not only optical anisotropy but the tenacity of the bond as well, as has been demonstrated in an earlier report (6).

Water, because of its high dielectric constant, causes a weakening of the bonds, and in this respect the process of water adsorption presents an analogy to heating, in which also the fine-structural bonds are lost (4). Indeed, clays in a highly swollen condition show a transformation of the smectic phase into the nematic one (5). At a still higher water content, when swelling passes into dissolution, no structure can be observed; one might conjecture, therefore, that structure characterizing the mesomorphous condition is present. In this case we observe only a diffuse, irregularly distributed double refraction determined by the anisotropy of colloidal particles.

The mechanism of swelling, based on microscopic observations, is as follows. The aggregation of the separate groups of soil particles into structural units is not uniform. The position of the axes of the external particles differs from that of the axes of the inner particles. This layer at the interface may be regarded as a semipermeable membrane ["Schaumwände" of Quincke (3)] permeable to water but impermeable to non-polar liquids. The volume increase of the soil structural cell is due to the diffusion of water, as described by Quincke (3, p. 1043) for the structural cells of various colloids. The non-polar liquid does not penetrate through the membrane; consequently, there is no swelling (7).

The penetration of water through the surface layer of oriented particles is readily observable under the microscope. The best way to demonstrate this

is by the use of a mixture of quartz sand with a suspension of Na-clay and humate, representing a model of soil. A layer of this liquid mixture about 0.25 mm. thick is placed on a slide. To obtain an even layer of a given thickness it is convenient to use, as was done by Quincke (3) in his experiments, thin glass tubes upon which a cover-glass is laid. After drying, a structure similar to that already described, is formed. When a drop of water is placed beside the cover-glass by means of a pipette the end of which is drawn out into a capillary, one can easily observe how the water rapidly enters the spaces between the structural cells and slowly penetrates into the cells themselves. As a result of the penetration of water, the dimensions of the cell gradually increase, and this increase may be measured in the various directions with the aid of a micrometer.

If the packing of the particles constituting the surface layer is stable, no dissolution of the wall occurs because of the compression of the ion envelope, irrespective of the adsorbed cation. The structural cell is not destroyed. This explains the behavior of the so-called "water-tight" aggregates. If the particles at the interface are less stable, a partial or complete disruption of the aggregate takes place. According to the kind of cation saturating the soil, a more rapid or a slower dissolution will occur. Thus, the soil structural element with an undisturbed layer of packed particles at the interface shows a remarkable resistance to water. It is, therefore, easy to understand why the various methods of mechanical soil analyses require the application of an outside force, such as pulverizing, shaking, or boiling.

The non-polar liquid does not penetrate through the membrane, and the grouping of particles remains unchanged. But if the semipermeable surface layer is damaged at one point, for instance by piercing the preparation with a glass needle, the non-polar liquid will penetrate readily into the cell. It follows from this that the mechanical disruption of the surface layer of particles must lead to a levelling of the amounts of absorbed water and non-polar liquid. From this point of view it is possible to explain the earlier experiments of Tiulin (4) dealing with a comparison of the amounts of water and xylene absorbed by a structural soil in the process of a gradual destruction of its aggregates. It was found that with increasing fragmentation of the structural aggregates, achieved by grinding, the amounts of absorbed water and xylene were gradually levelled out until, in the finest aggregates, they became equal.

On the same grounds, the fragmentation of soil must cause a decrease of the swelling capacity [as was long ago noted by Williams (10)] and an increase in the absorption of water. Since in this case the reversibility of the phenomena was of special interest, the following experiments were arranged.

A sample of columnar solonetz was pulverized and screened through a 0.25-mm. sieve. After this the powder was put into glass tubes 3 cm. in diameter and with perforated porcelain bottoms, covered with filter paper. The tubes were filled to the same level, and the powder was always packed in the same way, which was verified by weighing. The average absorption of

water by the pulverized solonetz equaled 49.8 cc. per 100 cc. Preliminary saturation of the solonetz with Ca or Na ions changed the absorption of water but slightly in comparison with the initial material: the absorption equaled 48.8 cc. and 50.5 cc. for the samples saturated with Ca and Na respectively. The results of water absorption by the pulverized soil differed sharply from those obtained with undisturbed soil, the latter averaging 40.05 cc. (7). This difference in the absorption of water, which was to be expected, may be explained by the definite grouping of the individual particles and the structure of the surface layer. This is indicated also by the sharp change in the volume of swelling, which in pulverized soil dropped to 10 per cent, whereas in the structural one it reached 21.66 per cent (7).

If the colloids do not lose their elastic properties, when the water-saturated powder is dried, the "oriented" grouping of particles into aggregates, which determines cohesion, is restored. This is a phenomenon of the same order as the one observed in mixtures of sand, clay, and humus, described in part II (8). The restoration of the structure, in the sense of a definite arrangement of small and large particles in relation to one another, the compactness of their packing, and consequently their tenacity, must be first reflected in the absorption of water. One should expect that the amount of water absorbed by pulverized soil, dried after a preliminary saturation with water, would approach that absorbed by structural soil. The respective experiments corroborated this assumption. After the solonetz powder was saturated with water, the tubes containing the soil were dried in the open. The dried soil decreased in volume and acquired almost the initial firmness, as might be judged by its resistance to crushing. The dried soil readily separated from the tube, and several determinations of water absorption were made with it by the colloidion film method (7). It was found that the absorption capacity had changed markedly in comparison with that of the original pulverized samples and averaged 36.43 cc. (as compared with 49.8 cc. for pulverized soil) per 100 cc. of soil. This value approaches closely the value of water absorption by the natural soil with an undisturbed structure (40.05 cc.). Swelling also had increased: it had almost doubled in comparison with that of the powder, and averaged 19.04 per cent, thus approaching the swelling capacity of undisturbed soil (21.60 per cent). This observation points to an almost complete restoration of the structure.

THE INFLUENCE OF ELECTROLYTES

Solutions of electrolytes do not influence the process of structure formation, i.e., the definite orientation of the particles in relation to one another, though it might be expected that the introduction of electrolytes would cause the particles to unite more closely. The formation of spontaneous structures under the influence of molecular forces leads to the deformation of the ion envelope; this is especially true when the particles have a lamellar shape, as in the case of clay. It is equally easy, therefore, to obtain tenacious structures from

highly hydrated and from less hydrated clays, and from both Na- and Ca-clays. Salt solutions exert an influence only on irregularly, unstably grouped particles.

These conceptions check well with our earlier experiments with soil swelling in electrolyte solutions (8). The results are corroborated by observations concerning the mechanism of the absorption of salt solutions by the soil structural cell. The process is analogous to the penetration of distilled water, and the picture of the disruption of the oriented surface layer observed in the case of an unstable grouping is similar to that obtained with distilled water.

It was to be expected, also, that the absorption of salt solutions by a pulverized soil would not differ from that of distilled water. It was assumed that preliminary saturation of a pulverized soil with a salt solution, such as $CaCl_2$, and its subsequent drying would not increase cohesion in comparison with the original material, since the orientation of particles depends on surface tension,

TABLE 10

Comparison of the absorption of water and $CaCl_2$ solutions by pulverized solonetz and by the same solonetz with an undisturbed structure

CONCENTRATION OF THE SOLUTION	AMOUNT OF SOLUTION ABSORBED, PER 100 CC. OF POWDERED SOIL	AMOUNT OF SOLUTION ABSORBED PER 100 CC. OF UNDISTURBED (NATURAL) SOIL	AMOUNT OF SOLUTION ABSORBED, AFTER PRELIMINARY SATURATION WITH $CaCl_2$ AND SUBSEQUENT DRYING, PER 100 CC. OF SOIL
	cc.	*cc.*	*cc.*
Distilled water	49.8	40.05	36.43
0.1 *N* $CaCl_2$	51.2	41.58	38.09
0.5 *N* $CaCl_2$	48.36	.....	36.04
1.0 *N* $CaCl_2$	46.9	39.17	34.89

which for a 0.1 *N* solution of $CaCl_2$ is almost the same as for water. The experiments corroborated this assumption. The same pulverized solonetz was saturated with $CaCl_2$ solutions of varying concentration and then dried in the open. In the dried samples the absorption of water was determined by the collodion film method. The results are shown in table 10.

The presence of $CaCl_2$ does not affect the restoration of structure; the values of the absorption of solutions of this salt do not differ from that of pure water.

The results on swelling in solutions of electrolytes are in harmony with the observations already mentioned, that the addition of $CaCl_2$ to Na-clay or Na-humate does not affect the precipitation of a smectic structure. Neither does the substitution of Ca for Na in clay or in humus affect in any way the formation of structure. It was to be expected that the swelling of clay in salt solutions would show the same characteristics of the aggregate condition as does swelling in pure water. Several experiments were arranged to determine swelling in solutions of salts ($CaCl_2$, $MgCl_2$) and in sulfuric acid. For the sake of comparison, we used 0.1 *N* and 1.0 *N* solutions. Samples of

different clays were allowed to swell for 20 days in these solutions. For the clays, without exception, the appearance of the nematic phase proved characterisitic (plate 3); a similar phenomenon was observed with pure water. In the gypsum plate of the first order it was possible to see a different coloring of the various sections of the preparation, changing with the rotation of the microscope stage; this indicates the phenomenon of twinning. The same phenomenon was observed in the experiments with pure water. It is noteworthy that in the 0.1 *N* solution of H_2SO_4 the optical sign of double refraction changed from negative to positive.

SUMMARY

Water absorption and swelling of soil are determined by the structure of the surface layer of oriented particles.

Particular importance is attached, in the case of unstable groupings, to the compactness of the particles at the interface solid phase-air. Mechanical damaging of the surface layer leads to disintegration.

From the viewpoint of the new conceptions concerning soil structure it becomes necessary to revise the theory of soil morphology. There is no other field—as has been justly noted by Vorländer—in which the internal relation between the shape of the molecule and the crystal would appear with such clearness as in the mesomorphous state.

REFERENCES

(1) Norton, F. H., and Hodgdon, F. B. 1932 Some notes on the nature of clay. *Jour. Amer. Ceramic Soc.* 15: 195.

(2) Nutting, P. G. 1927 Some mechanical properties of moist granular solids. *Jour. Wash. Acad. Sci.* 17: 185.

(3) Quincke, G. 1902 Die Oberflächenspannung an der Grenze wässeriger Colloidlösungen von verschiedener Conzentration. *Ann. Phys.* [Leipzig] (4F) 9: 969–1045.

(4) Rinne, F. 1933 Investigations and considerations concerning paracrystallinity. *Trans. Faraday Soc.* 29: 1016–1032.

(5) Sideri, D. I. 1936 On the formation of structure in soil: I. The structure of soil colloids. *Soil Sci.* 42: 381–393.

(6) Sideri, D. I. 1936 On the formation of structure in soil: II. Synthesis of aggregates; on the bonds uniting clay with sand and clay with humus. *Soil Sci.* 42: 461–481.

(7) Sideri, D. I. 1936 Soil swelling: I. The swelling of soil in water considered in connection with the problem of soil structure. *Soil Sci.* 41: 135–151.

(8) Sideri, D. I. 1936 Soil swelling: II. Swelling of soil in solutions of electrolytes. *Soil Sci.* 41: 275–293.

(9) Tiulin, A. F. 1929 Some questions of soil structure: III. [Russian] *Perm. Selskokhoz. Opyln. Stanzia*, No. 3.

(10) Williams, W. R. 1897 Lectures on Pedology [Russian]. Moscow.

PLATE 3

MICROPHOTOGRAPHS OF THE SWELLING OF CLAY IN CHLORIDE AND ACID SOLUTIONS

FIG. 1. Swelling of clay in a 1.0 *N* solution of $CaCl_2$. Nematic phase. Polarized light. Magnification × 27.

FIG. 2. Swelling of clay in a 1.0 *N* solution of $MgCl_2$. Nematic phase. Polarized light. Magnification × 27.

FIG. 3. Swelling of clay in a 0.1 *N* solution of H_2SO_4. Nematic phase. Polarized light. Magnification × 27.

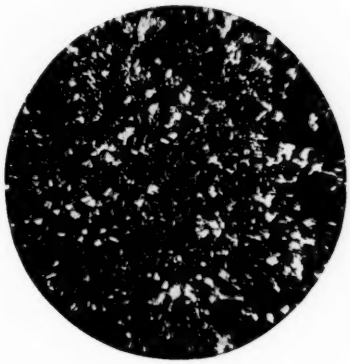

FIG. 1

FIG. 2

FIG. 3

ASSOCIATIVE AND ANTAGONISTIC EFFECTS OF MICROORGANISMS: I. HISTORICAL REVIEW OF ANTAGONISTIC RELATIONSHIPS[1]

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Nature provides numerous instances of associative and antagonistic relationships between different living systems. Among the most significant of these are the effects of the lower or microscopic forms of life upon the higher plants and animals and upon one another. The production by microorganisms of toxins specific against higher forms of life, as well as the general problem of parasitism, has received considerable attention in recent years. Much emphasis has been laid upon the symbiotic relationships between plants and microorganisms, comprising such phenomena as legume symbiosis and mycorrhiza formations. An extensive literature has also accumulated concerning the specific effects, either favorable or unfavorable, of microorganisms upon one another. In some cases these are due either to the consumption or modification of the food supply; in others, to changes in the physicochemical condition of the medium, especially reaction and oxidation-reduction potential; in still others, to the production of specific substances which are either toxic or stimulating to the growth of other organisms. The specific nature of these substances is still little understood, some being thermolabile others thermostable, some simple and others complex.

Since Pasteur (77) first propounded in 1863 the principle of microbic association as applied to the coexistence of aerobic and anaerobic organisms in nature, numerous investigations have been made on microbial associations. Many of these investigations were concerned with the influence of aerobic organisms in reducing the oxygen tension for the growth of anaerobes (74), others considered the significance of associations from a physiological or medicinal viewpoint (10, 44), or the significance of these phenomena in soil processes (72). In view of the fact that the associative relationships have thus been extensively reviewed, the following discussion will be limited to a summary of our knowledge of the antagonistic influences of microorganisms.

HISTORICAL

The study of the mutualistic influences of microorganisms, usually bacteria and fungi, has been carried out largely upon artificial substrates. A pure

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culture of an organism was inoculated upon an artificial medium; after several days incubation, another organism was added and the specific effect was determined. In some cases one form was inoculated directly into an agar substrate while the other was streaked on the plate after the medium had solidified. Frequently the specific substance or culture of antagonizing organism was added to the medium before or after sterilization, and the test organism was inoculated. In the case of fungi, the germination of spores and the development of the mycelium were usually used as criteria for the specific action.

The specific effects of the various organisms tested were found to vary considerably, depending on their nature, conditions of nutrition, and specific medium. In many cases, only a general antagonistic action has been demonstrated, whereas, in a few instances, an attempt was made to determine the nature of the specific substance produced and to study the conditions favoring its formation and destruction. Numerous attempts have been made to utilize this phenomenon in animal inoculation since Pasteur first inoculated, in 1877, *B. anthracis* together with various bacteria and demonstrated that the production of the specific disease in sensitive animals was repressed (56, 82); however, no clinical system of utilizing this relationship has as yet been developed.

More recently, attention has been directed to the influence of soil-inhabiting saprophytic microorganisms in repressing or modifying the action of plant pathogens. A number of interesting relationships between the different organisms have been established as a result of these investigations. However, the mutual relations of the numerous members of the soil microbiological population have been insufficiently studied. This is especially important, since microorganisms in soils and in composts carry out their numerous activities not in pure culture but as mixed populations.

The extent of development of any one group of microorganisms which inhabits a natural substrate, such as soil, compost, sewage, or water, depends upon a number of factors. Chief among these are the following:

1. Food supply, both quantitative and qualitative. The presence of certain specific nutrients favorable for the development of the particular organisms will markedly affect their growth. In some cases there is considerable competition for the available food material, and only those organisms develop which possess a specific capacity of attacking the particular compounds or which produce substances injurious to other organisms; in other cases, as when sulfur or ammonium salts are added to the soil, the organisms capable of utilizing these are so highly specific as to be able to grow as readily as if they were in pure culture.

2. Environmental conditions, favorable or unfavorable to the development of the specific organisms, notably temperature, oxygen supply, moisture content, reaction, soil structure, and abundance of organic matter.

3. Presence and abundance of other organisms which may produce substances that are either stimulating or toxic to the organisms in question or which may compete with them for the available nutrients. The modification of the population of a natural substrate, as in the case of the soil, by introducing new organisms or by specific treatment, whereby certain organisms are destroyed, is highly significant in this connection.

4. The presence of other organisms which are parasitic or phagocytic upon the particular forms. The rôle of protozoa in controlling bacterial activities by consuming the cells of the specific organisms has aroused considerable attention, and the significance of this phenomenon is still a matter of speculation.

Although this summary is limited to a discussion of the antagonistic effects of microorganisms, no attempt will be made to review all of the most extensive literature. Attention will be directed here only to those contributions which have a bearing, directly or indirectly, upon the problem under consideration.

Antagonistic action of fungi. Raulin (86) was the first to demonstrate, in 1869, that, in the course of development of a fungus upon a culture medium, changes are brought about in the latter which make conditions more favorable for the subsequent growth of the same organism. This was confirmed more recently by Nikitinsky (73), who has shown, however, that under certain conditions of nutrition this effect may be masked by other influences such as changes in reaction. On the other hand, Duclaux (23) demonstrated that the growth of a fungus upon a certain medium renders the latter more and more unfavorable for the same organism when it is freshly inoculated into the medium. These seeming discrepancies were explained by the work of Küster (54) and Lutz (62), who found that fungi produce not only growth-promoting but also growth-inhibiting substances. Fulton (33) suggested that the tendency of fungus hyphae to turn from the region in which hyphae of the same kind were growing is due to a negative reaction to chemical substances produced by the growing fungus.

De Bary (20) was the first to emphasize, in 1879, the significance of the antagonistic relationships of microorganisms; when two organisms were grown on the same substrate, one was found, sooner or later, to overcome the other and even kill it. This relationship was designated by Ward (101) as "antibiosis." It was explained (53) by the fact that when two organisms are capable of utilizing the same nutrients, but are differently affected by environmental conditions (reaction, air supply, temperature), the one organism that finds the conditions more suitable develops more rapidly and thus depresses the other. Numerous observations have since been reported concerning the preferential development, in various natural processes, of some organisms over others.

Many organisms are capable of producing substances which are injurious to their own development (*iso-antagonistic*) and even more so to other organisms growing close to them (*hetero-antagonistic*). This is largely the reason why certain fungi and bacteria are capable of growing in practically pure cultures even in a non-sterile environment. It is sufficient to cite the production of lactic and butyric acids by the corresponding bacteria, of citric acid by *Asp. niger*, of lactic acid by species of Rhizopus, of alcohol by yeasts, etc. These substances, as well as a great number of other compounds which, for lack of more exact information, are usually designated as lethal or growth-inhibiting, have frequently been looked upon as protective metabolic products produced by microorganisms in their struggle for existence. They play a highly sig-

nificant part in the life of microorganisms, especially those that grow parasitically upon living systems.

Some of the antagonistic substances are destroyed by boiling (54), by exposure to light, and by filtration (62), whereas others are resistant to heat and to ultra violet rays and are readily adsorbed by certain filters, from which they can be removed by the use of special solvents, such as ether, alcohol, chloroform, acetone. By means of these procedures, it was possible to differentiate between the substances which are antagonistic and those that are stimulating, both produced by the same organism (75). Reinhardt (89) found that the hyphae of *Peziza* will kill certain Mucorales, whereas different species of *Aspergillus* (*A. niger*, *A. flavus*) and *Penicillium* are able to kill *Peziza*. Wehmer (102) found that a single spore of *Pen. luteum* is capable of germinating in *Citromyces* cultures and of bringing about later the destruction of the latter. The production by *Pen. luteum purpurogenum* of a thermostable substance soluble in ether and in chloroform and antagonistic to the growth and acid production of *Asp. niger* has also been reported (76). In some cases, no relation could be observed between the active acidity produced by fungi and their ability to influence the growth of other organisms (106); in other instances, as in the case of the mutualistic influences of *Sclerotium rolfsii* and *Fusarium vasinfectum*, it was found (91) that at pH values below 6.9 the former completely overgrew the latter, whereas in alkaline ranges the reverse process took place.

In addition to the stable, enzyme-like bacteriolytic agents produced by fungi, other substances, non-enzymatic in nature and capable of suppressing bacterial development, are formed. Certain Penicillia, notably representatives of *P. chrysogenum*, were found (30) to produce a substance designated as *penicillin*, which has a strong antibacterial action. Gram-negative bacilli were least sensitive, while pyogenic cocci were most susceptible. The production of the substance reached its maximum in 7 days at 20°C. It was soluble in alcohol but not in ether and chloroform. It was found (15) to be inactivated by oxidation and by evaporation at 40–45° in acid and alkaline solutions, although it was fairly stable at pH 5–6. Light, oxygen, hydrogen, and carbon dioxide either prevented its formation or brought about its rapid destruction. Its action upon specific bacteria was of special interest, different non-related organisms being affected; this antibacterial substance was not identical with the pigment produced by the same fungus (88).

The formation of thermostable mutually inhibiting substances by *Helminthosporium sativum* and a bacterium has also been demonstrated (9). The bacterium and its products inhibited the growth of this fungus as well as of other members of the same genus, but not of *Fusarium conglutinaus*. The production of antibodies by the common edible mushroom *Psalliota campestris* against the fungus *Mycogone* has also been established (13).

It has been found in some of the early studies on the antagonistic effects of fungi that the formation or intensification of a pigment by one organism is

connected with its destructive action upon another. According to Doebelt (22), *Pen. africanum* produces a more intense pigment in contact with other fungi, such as *Asp. niger*; this pigment accumulates in the mycelium of the latter, which may thereby be killed. Nadson (68, 69) demonstrated that some fungi (*Pen. luteum* and *Spicaria purpurogenes*) produce a pigment which is used not only for purposes of protection but also for attack upon other organisms, whereby the latter are killed and stained.

Similar observations were made with bacteria. Horovitz (45) reported that the cholera vibrio produces, in the presence of *Sarcina lutea*, a dark violet pigment accompanied by an increase in agglutination and virulence. The destruction of *Dictyostelium mucoroides* by a red-pigment forming bacterium (*B. kieli*), accompanied by intense pigment formation, has also been established (79); the blue pigment of *Bact. violaceus* only delayed the growth of the fungus; on the other hand, *Bact. fluorescens liquefaciens* was found to be digested by the myxomycete living with it in a form of symbiosis.

Harder (39), in a study of the behavior in mixed culture of fungi belonging to the Basidiomycetes and Ascomycetes, found that young colonies do not produce so much of the toxic principle as do older ones, hence they can grow close to one another. *Coniophora cerebella* was held back by *Pen. glaucum*, its mycelium being considerably modified; in time, the former organism adapted itself to the latter and overgrew it, its rate of growth being eventually more rapid than that of a pure culture. The toxic principle was produced in varying degrees by different fungi; it was either temporary or permanent and was found more among the lower fungi or molds rather than in the Basidiomycetes. The toxic substance either modified or actually killed the mycelium of the other fungus, or prevented spore germination; it was partly destroyed by boiling. A number of different fungi were shown (2) to have a specific influence upon the germination of certain ascomycetes.

The question of staling of media in which certain fungi have been growing has received considerable attention. The growth of *Fusarium* on different media results in the production of both thermolabile and thermostable toxic substances (6). The staling effect was not specific, since spores of *Botrytis cinerea* were found to be more susceptible to the metabolic products of *Fusarium* than were the spores of the latter. This effect was partly removed by boiling and by correction of the alkaline reaction of the medium. According to Pratt (81), ether removes the substance causing staleness, after acidification of the medium; a similar effect was produced by treatment with colloidal clay. The accumulation of basic substances in the medium was shown to be largely responsible for the staling (9, 81).

Antagonistic action of yeasts. The production of specific antagonistic and stimulating substances has also been demonstrated for yeasts. Fernbach (29) found, for example, that certain yeasts produce volatile substances which are toxic not only to other yeasts but also to bacteria. Okunuki (75) demonstrated that rose yeasts (*Torula suganii*), either fresh or heated to 120°–

130°C., contain substances which act antagonistically upon fungi, especially upon young mycelium, but not upon yeasts: the growth of *A. niger* was reduced by 60–70 per cent and that of *A. oryzae* by 25–30 per cent. The toxic substances were not found in the ash and were not secreted in the filtrate, but remained in the yeast cells; an alkaline reaction was unfavorable to the formation of these substances and to their action. The yeast also produced a growth-promoting substance which was thermolabile; it was found in the filtrate and was not affected by an alkaline reaction. The antagonistic substance was soluble in acetone, ethyl alcohol, ether, and chloroform and was adsorbed by kaolin, on a Seitz filter, by filter paper, and by fungus mycelium; it could be removed from the kaolin by ether or acetone. Acetone-treated yeast had no longer an antagonistic effect but only a stimulating one. The injurious effect of the substance was overcome after 12 days growth of the fungi and was actually followed by a stimulating effect.

Pulkki (83), by boiling yeast, obtained a substance which stimulated the growth of *Bac. mycoides* in a medium containing peptone, glucose, and minerals; its concentration was parallel to that of the nitrogen content of the medium. Peptone and impure sugar were also found to contain some of the substance. An extensive literature has accumulated concerning the production by yeasts of growth-stimulating or "bios" substances, which is beyond the scope of this review.

Antagonistic action of bacteria. The investigations on the antagonistic effects of bacteria on other organisms have been largely limited to pathogenic forms. *Bact. pyocyaneum* and *Bact. fluorescens* have received particular attention. It is sufficient to mention, among the earlier investigations, the work of Garre (34) and Nencki (71), and later that of Löde (60) and Pringsheim (82), and more recently that of Lasseur and associates (56). The production by bacteria of thermolabile substances injurious to their own subsequent growth and to that of other bacteria has thus been established, as shown by the work of Eijkman (24–25) and of many others (10, 53).

Various solid and liquid media have been utilized in these investigations. Nencki (71) reported that when two bacteria are planted simultaneously, metabolic products are formed which would not take place in pure culture, and that certain decomposition processes are either hastened or retarded. Löde (60) isolated a micrococcus which had an antagonistic effect upon various microorganisms at a distance of three or more cubic centimeters, the active substance being dialyzable. Rahn (85) and Eijkman (25) demonstrated that certain bacteria are favored by their own metabolic products, whereas other products have an adverse effect; the first are thermostable and non-filterable, and the second are thermolabile (at 60 to 100°) and are destroyed by light. According to Pringsheim (82), *Bac. mesentericus vulgatus* has an antagonistic effect upon *B. diphtheriae*. Several giant colonies of the latter were formed within the zone of the antagonizing organism; it was suggested that the substance produced by the latter is in the nature of a poison, which stimulates

in small doses and is injurious in larger doses. The poisonous substance was thermolabile.

Wolf (105) has shown that the activity of the influenza organism is largely dependent on the presence of accompanying bacteria, some (micrococci) being favorable to its growth and others (*Bact. pyocyanum*, *Bac. subtilis*) injurious. According to Lasseur (56), the mutual growth of two organisms modifies considerably their morphology and pigment production. The inhibiting action of some bacteria upon others is complex in nature; it is more than a result of a change in pH value and in oxidation-reduction potential, of surface tension, and of "action at a distance," in accordance with Gurewitch's conception. The simultaneous growth of *Staph. aureus* and *B. coli* was found (87) to be injurious to the former and not to the latter; this effect was increased by an increase in the number of cells of *B. coli* in the inoculum. The competition for the available nutrients was suggested as the possible explanation of this phenomenon. *Serratia marcescens* was shown (26) to produce a thermostable substance antagonistic to diphtheria, gonococci, and a variety of other bacteria; its activity increased with age of culture; it was not a lipid and was not associated with pigment production.

Antagonistic relationships among the soil microörganisms. The soil is inhabited by numerous microörganisms which are living in a state of mutual equilibrium (100). Any modification of this equilibrium results in a number of changes in the population, both quantitative and qualitative in nature. This population offers a number of illustrations of interrelationships which are of distinct interest in understanding not only the specific ecological nature of the population under a certain set of conditions (biocoenosis), but also the resulting activities of this population. Because of the complexity of this population, it cannot be treated as a whole, but certain relationships of different organisms can be isolated and examined separately. The interrelationships of certain groups of the microbial population of the soil have received particular attention. It is sufficient to direct attention to the relations between non-spore-forming bacteria to the spore-formers, of actinomyces to bacteria, of certain fungi to other fungi, of bacteria to fungi and *vice versa*, and finally, of protozoa to bacteria.

Conn and Bright (16) found that when *Bac. cereus* and *Bact. fluorescens* were inoculated simultaneously into sterile manured soil, the former failed to develop, while the latter grew abundantly. Lewis (58) reported that *Bact. fluorescens* repressed the growth of *Bac. mycoides* and of other spore-forming bacteria and micrococci; *Bact. aerogenes* and *Serratia marcescens* were highly resistant; fungi were not inhibited; yeasts were inhibited only to a limited extent; and actinomyces were more sensitive. Lewis also confirmed the previous results of Löde (60) that the production of bactericidal and inhibitory substances by bacteria depends on the amount of available oxygen; these substances were found to be thermostable and to be adsorbed by charcoal (38) and by soil (58); this led Lewis to conclude that a toxin of this type does not persist in the soil.

Greig-Smith (36, 37) demonstrated in 1917 that various actinomyces are capable of producing substances toxic to soil bacteria; the fact that actinomyces grow very slowly in soils appeared to him as suggesting the possibility that they comprise the factor limiting bacterial development; the fact, however, that they withstood toluene treatment spoke against such a possibility. Lieske (59) found that certain actinomyces are antagonistic to *Staphyl. pyogenes* but are repressed by other bacteria; namely, *Staphyl. albus*, *Bact. prodigiosum*, and *Bact. pyocyaneum*. The last organism, because of its capacity to produce *pyocyanase*, a bacteriolytic substance, was claimed by some investigators to vaccinate the substrate against the growth of other microörganisms (90). Lewis (58) also found that spore-forming bacteria isolated from soil could be repressed in their development by different actinomyces.

Borodulina (5) demonstrated that a toxic substance is produced by actinomyces, the action of the toxin being reduced in alkaline and increased in acid media; not only was the morphology of the bacterium thereby modified, as shown by a lack of spore formation and elongation of cells, but also its physiology, as shown by a reduction in the capacity to liberate ammonia from proteins. When *B. mycoides* and the actinomyces were inoculated together in peptone media, no toxic action was exerted, because the former changed the reaction rapidly to alkaline, thus making conditions unfavorable for the production of the toxin by the actinomyces. The phenomenon of antagonism, at least in the case of actinomyces, may in some way be related to the formation of "phage" or self-destructive substances. It was recently shown (104) that certain actinomyces can produce lytic agents, which are capable of exerting a lytic effect not only upon actinomyces, but also upon other organisms. The antagonistic action of some actinomyces against others has also been established (63a); the more aerobic species were found to be antagonistic to the less aerobic forms.

The possibility that excessive variation in the number of bacterial colonies on the plate may be due to the development of certain soil organisms which exert a toxic influence on the other forms was suggested by Fisher, Thornton, and MacKenzie (29a).

The antagonistic interrelationships existing among the microörganisms comprising the microbiological population of the soil have received particular attention from the point of view of the modification of the virulence of plant pathogens that find temporary or permanent habitat in the soil. Bamberg (3) isolated certain cultures of bacteria which inhibit the development of *Ustilago zeae;* these bacteria were capable of destroying the colonies of various smut fungi; it was suggested that the wide-spread distribution of such bacteria might bring about a check on the multiplication of the fungus in the soil. Four types of bacteria antibiotic to the smuts and to certain other fungi were described (48); some of the bacteria were found to produce enzymes which were able to dissolve the chemical contituents of the cell walls of the fungus sporidia; it was shown that the bacteria act also upon the specific fungi in the soil.

Chudiakov (14) isolated two bacteria which were capable of bringing about the lysis of different species of *Fusarium* and other fungi. These bacteria were found widely distributed in the soil; they were absent, however, in certain flax-sick soils, in spite of the abundance of *Fusarium*. When this organism was introduced into soils containing the active bacteria, the fungus did not develop and plant disease did not occur.

The above bacteria destroyed the fungus through a specific lytic effect. Certain other bacteria, however, were found to prevent the injurious action of the plant pathogen by direct repression, as shown by Porter (80) for *Helminthosporium* on wheat. According to Sanford and Broadfoot (94), the virulence of the root-rot of cereals, *Ophiobolus graminis*, can be completely controlled by the activities of various soil-inhabiting microörganisms; filtrates of these organisms were nearly as effective in repressing the pathogen as were the living organisms. The reduction of potato scab by plowing under a green rye crop has been explained by Sanford (93) and by Millard (66) as due to the development of other organisms, such as saprophytic actinomyces, which suppress the growth of the pathogenic *Act. scabies*.

Various other experiments point to the possibility of suppressing the growth and infectiveness of the plant pathogens by the activities of different soil microörganisms. It is sufficient to cite further the suppression by various specific fungi and bacteria of the pathogen *Monilia fructigena* on apples (98), *Fusarium culmorum* and *Helminthosporium sativum* on wheat (4, 41), *P. omnivorum* on cotton (50), *Rhizoctonia solani* and *Phytophthora parasitica* on citrus seedlings; the last two pathogens are markedly influenced by the growth of a common soil saprophyte *Trichoderma lignorum* (1, 4, 102a). A species of *Trichoderma* could also cause a reduction in the amount of Texas root-rot of watermelons caused by *Phymatotrichum omnivorum* (8). Different fungi belonging to the *Hypochnus* and *Sclerotium* groups were shown to cease to be pathogenic in the presence of other organisms (27). *Pythium*, parasitic on sugar cane, was found (97) to be antagonized by a number of soil actinomyces; the inoculation of sterilized soil with these actinomyces reduced considerably the infection of the cane; the toxic principle was partially destroyed by heat. The antagonistic action of a large variety of soil organisms, comprising fungi, actinomyces, bacteria, and protozoa, to different plant pathogens causing soft rots of vegetables was suggested by Hino (43). Those organisms were found to produce soluble substances which have a lethal effect upon the pathogens (1, 102a).

An increase in temperature (35, 41) favors infection of wheat seedlings with *Ophiobolus graminis* in sterilized soil; however, in unsterilized soil, higher temperatures, by favoring the antagonistic effects of the soil microflora, repress the development of the plant pathogen. Antagonism was found to be lowest in poor soils with a limited organic matter content and smaller numbers of microörganisms, and was highest in fertile soils with a high organic matter content (35, 67). The inoculation of steamed soil with various saprophytes

was found (40) to result in a decrease of the parasitic activity of *Pythium debaryanum* upon forest nursery seedlings. The "biological control" of various soil-borne diseases, suggested by Garrett (35) and others (57), which consists in modifying the soil so as to encourage the maximum development of the antagonizing saprophytic soil population, is thus shown to have a sound foundation (66). Weindling and Fawcett (103) demonstrated that inoculation of sterilized soil with the saprophytic soil fungus *Trichoderma* will prevent infection of citrus seedlings by the pathogenic *Rhizoctonia*.

Soil toxins. The soil microflora and microfauna exert antagonistic effects not only upon microorganisms injurious to plants and to animals, but also upon the beneficial soil microorganisms. The exact nature of this effect is still obscure. Different theories have been proposed to explain its significance in soil processes and plant growth. These comprise the "toxin" theory of soil fertility, the production of a bacteriophage in certain "sick soils," the rôle of protozoa in controlling bacterial activities in soil, etc. In most cases, these theories proved to be either completely unjustified, or only of local significance, or, as experimental evidence accumulated, the results could be interpreted differently.

It seems to be definitely established that some organisms exert a decided antagonistic effect toward certain important soil bacteria, as in the case of the root nodule bacteria (52). There has also accumulated sufficient evidence that substances toxic to bacteria or so-called "bacterio-toxins" may be formed under certain conditions. Substances toxic to the growth of *Bact. prodigiosum* were demonstrated by Greig-Smith (36); these substances, produced by different soil microorganisms, were partly or entirely destroyed by heat, sunlight, and storage. Hutchinson and Thaysen (47) concluded that toxic substances found in pure culture of microorganisms are different from the soil toxins. Lewis (58) demonstrated that certain soil organisms produce in culture media substances which are toxic to other organisms. He concluded, however, that the accumulation in soils of free bacterio-toxins in sufficient amounts to inhibit the growth of bacteria was highly problematical; he suggested that differences in the nutritive requirements and relative growth rate, rather than inhibition due to toxic metabolic products, could account for the differences in the number of bacterial cells reported by other investigators. These conclusions were based on the study of autoclave-heated soils; when *Bact. fluorescens* was grown in manured soil and an extract prepared by means of alcohol, a substance was obtained which proved to be toxic to a number of bacteria including *Bac. cereus*, *Bac. mycoides*, *Bac. anthracis*, and *Sarcina lutea;* control soil cultures sterilized, but uninoculated, failed to yield a toxin; the toxin was adsorbed by the soil and was not removed by water.

Two other products of microbial life, not strictly "toxins," as the term is commonly understood, must be included here, namely, (a) specific bacteriophages, and (b) substances which have a specific inhibiting effect upon certain organisms, as in the case of hydrogen peroxide for anaerobic bacteria. An

extensive literature has accumulated on the production of specific lytic substances by various bacteria and actinomyces including a large number of soil organisms. It is sufficient to call attention to the fact that this "phage" may be found abundantly in soil and may become responsible for the destruction of certain important soil bacteria, thus leading to a condition of "soil sickness," as in the case of the alfalfa- and clover-sick soils (21). Bacteria sensitive to hydrogen peroxide (anaerobes) are injured by the presence of organisms producing this substance but will be assisted by other organisms, as various aerobic bacteria, producing catalase (44).

The possibility that certain amino acids, as tryptophane, produced by various bacteria may be toxic to other organisms, has also been demonstrated (44). The stimulating effect of mycorrhizal fungi on the host plant has been explained (31) by their capacity to inactivate, destroy, or absorb certain plant retarding principles found among the organic constituents of peat and other humus formations and in fungi.

Rôle of protozoa in controlling the microbiological population of the soil. "The protozoan theory of soil fertility," originally based upon the fact that the capacity of protozoa to consume soil bacteria is responsible for the infertility of certain soils has recently been considerably modified. The results of recent investigations have been interpreted in terms totally opposed to those originally suggested by Russell and Hutchinson (92). When protozoa were introduced into cultures of various specific bacteria concerned in certain known important soil processes (13, 14), they were found able to feed upon these bacteria, bringing about considerable reduction in their numbers; however, this capacity was not necessarily accompanied by a detrimental effect upon the specific processes brought about by the bacteria in question; the effect was in many cases actually beneficial (17, 18, 64, 70). Cutler and Crump (19) have, therefore, reversed the original conception of the originators of the protozoan theory and have suggested that the presence of protozoa in the soil keeps the bacteria at a level of maximum efficiency.

The earlier hypothesis (92) of the rôle of protozoa in soil fertility was based upon the changes in bacterial numbers and activities as a result of partial sterilization; the conclusion was reached that, in normal soils, protozoa keep bacterial development in check; when the protozoa are destroyed by heat or by chemicals, the bacteria begin to multiply rapidly; this leads to more active decomposition of the organic matter, to greater liberation of nitrogen, and to improved soil fertility. This explanation was based upon several assumptions which were not fully justified; namely, (a) that bacteria are the only important soil organisms responsible for the decomposition of the organic matter; it has been repeatedly shown that this is not the case; (b) that protozoa, by consuming some of the bacteria, especially those decomposing organic matter and forming ammonia, with which those investigations were largely concerned, restrict bacterial development and, *ipso facto*, organic matter decomposition. Further, the fact was overlooked that the soil harbors other

organisms, notably fungi and actinomyces, which could bring about the decomposition of plant and animal residues as well as of the soil humus and liberate the ammonia, even with the complete elimination of all the bacteria.

The more recent explanation of the influences of protozoa on soil processes (19), which result in stimulation of bacterial development and hence in accelerated transformation of soil materials, assumes also that the processes taking place in the soil are similar to those which are brought about in artificial culture media, an assumption which is still open to question; no consideration is given to the fact that the presence of numerous other organisms in the soil may modify considerably the activities of the protozoa, as one might be tempted to conclude from the results in artificial media. It has been shown (51), for example, that the use of such media gives a one-sided conception of the significance of protozoa in soil processes. Although the suggestions of Cutler (19) concerning the function of protozoa in the soil are based upon more direct experimental evidence, they are still inadequate, because they give insufficient consideration to numerous elements of the complex soil population.

The direct method of soil examination has revealed (51) the fact that protozoa make up only a small portion of the soil population, both in numbers and in the amount of cell substance. Their ability to reduce bacterial numbers in normal soil is very slight. The indirect method of studying protozoa in solution media, where the types developing and the activities resulting are quite different from those occurring in the soil, has been largely responsible for the exaggerated importance attached to these organisms. It is also of interest to call attention here to certain observations on the toxic action of different bacteria upon protozoa (12, 61, 78). In some cases, the protozoa were able to develop a certain resistance to the specific bacterial products (78).

Antagonistic relationships among microörganisms in sewage, water, and other natural substrates. This is not the place to discuss in detail the antagonistic effects of microörganisms carrying out their numerous activities in various other natural habitats, such as sea water, lake and river water, and sewage. Attention may only be directed to certain specific instances which have been given much consideration. These are cited because of their similarity to the processes reported for the behavior of soil organisms. The survival of *B. typhosus* received particular attention in the study of mixed populations in sewage. This organism was found (49) to survive for a much longer period of time in sterilized than in unsterilized tap water, the period being shortest in the case of plain river water. The presence of certain bacteria, notably *B. fluorescens*, was shown to reduce considerably the survival period of the pathogen (32). Sewage was further shown (42) to contain substances directly toxic to *B. typhosus*. It was also demonstrated that the destruction of this organism in sewage may be brought about by the numerous protozoa inhabiting this substrate (46, 96), a phenomenon which seems to be well recognized (84).

The production of bacteriolytic substances in sea water has also been definitely established (99, 107). Fresh water and sewage bacteria added to sea

water suffer rapid destruction; even cultures of marine bacteria added to the raw water will rapidly die out. The nature of the agents responsible for the destruction of the bacteria is a subject for further study.

Various other instances of antagonistic relationships of microörganisms are found on record. It is sufficient to mention, for example, the inhibiting action of various species of *Torulopsis* and bacteria toward the *Dematiaceae* which cause the blue staining of wood pulp (65). In the study of the influence of different organisms upon the decay of fruits, it was found (95) that in some cases decay was markedly increased even to the point of equivalency to the combined effects of both organisms; in other cases, decay was depressed by mixtures of organisms as compared with the most active forms; the type of decay was also modified. This depended on temperature and presence of specific organisms.

The marked antagonistic effects that have been observed in the case of various bacteria and fungi toward plant and animal parasites have been utilized, in numerous ways, for the practical control of the disease caused by these. Bacterial and yeast therapy, which consists in the utilization of cultures of lactic acid bacteria, yeast feeding, use of pyocyanase preparations, etc., are based upon this principle.

SUMMARY

A survey of the literature on the antagonistic relationships of microörganisms, with special reference to those that make up the complex soil population, reveals certain important pertinent facts, which can be summarized as follows:

Numerous organisms, comprising bacteria, fungi, actinomyces, and protozoa, bring about injurious or destructive effects upon themselves or upon other soil organisms.

In some cases the injurious effect may be due to competition for nutrients, in other cases it is due to a change in the environmental conditions of the substrate, especially oxidation-reduction potential and reaction; more frequently, it is due to the formation of substances which exert a definite toxic effect.

The production of these toxic substances by various specific microorganisms is greatly influenced by the reaction, temperature, and aeration of the substrate, as well as by the presence of other organisms.

Evidence is still lacking as to whether these substances are accumulated in the soil, whether the organisms affected may not be able to overcome them, and whether they may not be destroyed by other members of the soil population.

Without questioning the significance of various specific interrelationships among microorganisms, no general theory based upon these "toxic" or "antagonistic" phenomena can be proposed before more information has accumulated concerning the mutualistic behavior of the numerous microorganisms which make up that complex but highly significant microbial population which inhabits the soil.

Some of the soil organisms, notably the protozoa, are able to destroy directly other members of the soil population, especially the bacteria; this phenomenon need not be injurious, however, to the specific processes brought about by these bacteria.

The claims concerning the effects of protozoa on soil processes, based upon their growth on artificial culture media, appear to be exaggerated.

The available information concerning antagonism among microorganisms may be useful

in explaining the behavior of various specific organisms; it is little more than suggestive, however, in explaining the mutualistic interrelationships of the numerous microorganisms comprising the soil population and the equilibrium condition normally found to exist in this population.

REFERENCES

(1) ALLEN, M. C., AND HAENSELER, C. M. 1935 Antagonistic action of Trichoderma on Rhizoctonia and other soil fungi. *Phytopath.* 25: 244–252.

(2) ASTHANA, R. P., AND HAWKER, L. E. 1936 The influence of certain fungi on the sporulation of *Melanospora destruens* Shear and some other Ascomycetes. *Ann. Bot.* 50: 325–344.

(3) BAMBERG, R. H. 1931 Bacteria antibiotic to *Ustilago zeae*. *Phytopath.* 21: 881–890.

(4) BISBY, G. R., JAMES, N., AND TIMONIN, M. 1933 Fungi isolated from Manitoba soils by the plate method. *Canad. Jour. Res.* 8: 253–275.

(5) BORODULINA, J. S. 1935 Interrelations of soil actinomyces and *B. mycoides*. *Microbiologia* 4: 561–586.

(6) BOYLE, C. 1924 Studies in the physiology of parasitism. X. The growth reactions of certain fungi to their staling products. *Ann. Bot.* 38: 113–135.

(7) BROADFOOT, W. C. 1933 Studies on foot- and root-rot of wheat. Effect of age of the wheat plant upon the development of foot- and root-rot. *Canad. Jour. Res.* 8: 483–491.

(8) BROWN, J. G. 1933 Watermelon susceptible to Texas root-rot. *Science* 78: 509.

(9) BROWN, W. 1923 Experiments on the growth of fungi in culture media. *Ann. Bot.* 37: 105–129.

(10) BUCHANAN, R. E., AND FULMER, E. I. 1930 Physiology and Biochemistry of Bacteria, vol. 3: 3–28. Williams & Wilkins Co., Baltimore, Md.

(11) CARTER, J. C. 1935 Diffusible nature of the inhibitory agent produced by fungi. *Phytopath.* 25: 1031–1034.

(12) CHATTON, E. AND M. 1923, 1929, 1925 L'influence des facteurs bacteriens sur la nutrition, la multiplication et la sexualité des infusoires. *Compt. Rend. Acad. Sci.* [Paris] 176: 1262–1265 (1923); 188: 1315–[redacted] (1929); *Compt. Rend. Soc. Biol.* [Paris] 93: 675–678 (1925).

(13) CHAZÉ, M., AND SARAZIN, A. 1936 Novelles données biologiques et experimentales sur la môle maladie du champignon de couche. *Ann. Sci. Nat. Bot.* (X) 18: 1–86.

(14) CHUDIAKOV, J. P. 1935 The lytic action of soil bacteria on parasitic fungi. *Microbiologia* 4: 193–204.

(15) CLUTTERBUCK, P. W., LOVELL, R., AND RAISTRICK, H. 1932 Studies on the biochemistry of microorganisms. XXVI. The formation from glucose by members of the *Penicillium chrysogenum* series of a pigment, an alkali-soluble protein and penicillin—the antibacterial substance of Fleming. *Biochem. Jour.* 26: 1907–1918.

(16) CONN, H. J., AND BRIGHT, J. W. 1919 Ammonification of manure in soil. *Jour. Agr. Res.* 16: 313–350.

(17) CUTLER, D. W., AND BAL, D. V. 1926 Influence of protozoa on the process of nitrogen fixation by *Azotobacter chroococcum*. *Ann. Appl. Biol.* 18: 516–534.

(18) CUTLER, D. W., AND CRUMP, L. M. 1929 Carbon dioxide in sands and soils in the presence and absence of amoebae. *Ann. Appl. Biol.* 16: 472–482.

(19) CUTLER, D. W., AND CRUMP, L. M. 1935 Problems in Soil Microbiology. Longmans, Green & Co., London.

(20) DEBARY, A. 1879 Die Erscheinungen der Symbiose. Straszburg.

(21) DEMOLON, A., AND DUNEZ, A. 1936 Nouvelles observations sur le bacteriophage et la fatigue des sols cultivés en luzerne. *Ann. Agr.* 6: 434–454.

(22) DOEBELT, H. 1909 Beiträge zur Kenntnis eines pigmentbildenden Penicilliums. *Ann. Mycol.* 7: 315–338.

(23) DUCLAUX, E. 1900 Traité de Microbiologie, vol. 1: 236; vol. 3: 519. Paris.

(24) EIJKMAN, C. 1904 Ueber thermolabile Stoffwechselprodukte als Ursache der natürlichen Wachstumshemmung der Mikroorganismen. *Centbl. Bakt.* [I] *Orig.* 37: 436–449.

(25) EIJKMAN, C. 1906 Ueber natürliche Wachstumshemmung der Bakterien. *Centbl. Bakt.* [I] *Orig.* 41: 367–369, 471–474.

(26) EISLER, M., AND JACOBSOHN, I. 1935 Über die antagonistische Wirkung steriler Bouillonextrakte aus Bacterium prodigiosus. *Ztschr. Hyg.* 117: 76–91.

(27) ENDO, S. 1931, 1932, 1933 Studies on the antagonism of microorganisms. I. Growth of *Hypochnus sasakii* Shirai as influenced by the antagonistic action of other microorganisms. *Bul. Miyazaki Col. Agr. For.* 3: 95–119 (1931); 4: 133–158, 159–185 (1932); 5: 51–73 (1933).

(28) FAWCETT, H. S. 1931 The importance of investigations on the effects of known mixtures of microorganisms. *Phytopath.* 21: 545–550.

(29) FERNBACH, A. 1909 Sur un poison élaboré par la levure. *Compt. Rend. Acad. Sci.* [Paris] 149: 437–439.

(29a) FISHER, R. A., THORNTON, H. G., AND MACKENZIE, W. A. 1922 The accuracy of the plating method of estimating the density of bacterial populations. *Ann. Appl. Biol.* 9: 325–359.

(30) FLEMING, A. 1929 On the antibacterial action of cultures of a Penicillium, with special reference to their use in the isolation of *B. influenzae*. *Brit. Jour. Exp. Path.* 10: 226–236.

(31) FREISLEBEN, R. 1935 Weitere Untersuchungen über die Mykotrophie der Ericaceen. *Jahrb. Wiss. Bot.* 82: 413–459.

(32) FROST, W. D. 1904 The antagonism exhibited by certain saprophytic bacteria against *Bacillus typhosus* Gaffky. *Jour. Infect. Diseases* 1: 599–640.

(33) FULTON, H. R. 1908 Chemotropism of fungi. *Bot. Gaz.* 41: 81–108.

(34) GARRE, C. 1887 Über Antagonisten unter den Bakterien. *Centbl. Bakt.* 2: 312–313.

(35) GARRETT, S. D. 1934, 1936 Factors affecting the severity of take-all. *Jour. Agr. So. Aust.* 37: 664–674, 799–805, 976–983; *Biol. Rev.* 9: 351–361 (1934); *Ann. Appl. Biol.* 23: 667–699 (1936).

(36) GREIG-SMITH, R. 1912, 1916 Contributions to our knowledge of soil fertility. IV. The agricere and bacteriotoxins of soil. *Proc. Linn. Soc. N. S. Wales* 36: 679–699 (1912); 40: 631–645 (1916).

(37) GREIG-SMITH, R. 1917 Contributions to our knowledge of soil fertility. XV. The action of certain microorganisms upon the numbers of bacteria in the soil. *Proc. Linn. Soc. N. S. Wales* 42: 162–166.

(38) GUNDEL, M. 1927 Ueber den Antagonismus von Coli-Bakterien auf Milzbrandbazillen. *Centbl. Bakt.* [I] *Orig.* 104: 463–473.

(39) HARDER, R. 1911 Über das Verhalten von Basidiomyceten und Ascomyceten in Mischkulturen. *Naturw. Ztschr. Forst. u. Landw.* 9: 129–160.

(40) HARTLEY, C. 1921 Damping-off in forest nurseries. *U. S. Dept. Agr. Prof. Paper Bul. 934.*

(41) HENRY, A. W. 1931, 1932 The natural microflora of the soil in relation to the foot-rot problem of wheat. *Canad. Jour. Res.* 4: 69–77 (1931); 5: 407–413 (1931); 7: 198–203 (1932).

(42) HEUKELEKIAN, H., AND SCHULHOFF, H. B. 1935 Studies on the survival of *B. typhosus* in surface waters and sewage. *N. J. Agr. Exp. Sta. Bul. 589.*

(43) HINO, I. 1935 Antagonistic action of soil microbes with special reference to plant hygiene. *Trans. Third Internatl. Cong. Soil Sci.* 1: 173–174.

(44) HOLMAN, W. L. 1928 Bacterial associations. *Newer Knowledge of Bacteriology and Immunology*, p. 102–119. Edited by Jordan and Falk.

(45) HOROVITZ, L. 1910 On the biology of cholera vibrios. *Arch. Biol. Nauk.* 16: 448.

(46) HUNTEMÜLLER, O. 1905 Vernichtung der Bakterien im Wasser durch Protozoen. *Arch. Hyg.* 54: 89–100.

(47) HUTCHINSON, H. P., AND THAYSEN, A. C. 1918 The non-persistence of bacteriotoxins in the soil. *Jour. Agr. Sci.* 9: 43–62.

(48) JOHNSON, D. E. 1931, 1935 The antibiosis of certain bacteria to smuts and some other fungi. *Phytopath.* 21: 843–863 (1931); *Sixth Internatl. Bot. Cong.* 2: 221–222 (1935).

(49) JORDAN, E. O., RUSSELL, H. L., AND ZEIT, F. R. 1904 The longevity of the typhoid bacillus in water. *Jour. Infect. Diseases* 1: 641.

(50) KING, C. J., AND LOOMIS, H. F. 1926 Experiments on the control of cotton root-rot in Arizona. *Jour. Agr. Res.* 32: 297–310.

(51) KOFFMAN, M. 1934 Die Mikrofauna des Bodens, ihr Verhältnis zu anderen Mikroorganismen und ihre Rolle bei den mikrobiologischen Vorgängen im Boden. *Arch. Mikrobiol.* 5: 246–302.

(52) KONISHI, K. 1931 Effect of soil bacteria on the growth of the root nodule bacteria. Kyoto Col. Agr. Mem. 16.

(53) KRUSE, W. 1910 Allgemeine Mikrobiologie, p. 161, Leipzig.

(54) KÜSTER, E. 1908 Keimung und Entwicklung von Schimmelpilzen in gebrauchten Nährlösungen. *Ber. Deut. Bot. Gesell.* 26a: 246–248.

(55) KÜSTER, E. 1909 Über die chemische Beeinflussung der Organismen durch einander. *Entwicklungsmechanik der Organismen*, H. IV. Edited by W. Roux. Leipzig.

(56) LASSEUR, PH., AND MARCHAL, J. G. 1934, 1936 Associations bacteriennes. Antagonisme-Antibiose. *Trav. Lab. Microbiol. Facult. Pharm. Nancy*, 7: 75–89, 91–104 (1934); 9: 49–53 (1936).

(57) LEEMANN, A. C. 1931 The problem of active plant immunity. *Centbl. Bakt.* [II] 85: 360–376.

(58) LEWIS, J. M. 1929 Bacterial antagonism with special reference to the effect of *Pseudomonas fluorescens* on spore forming bacteria in soils. *Jour. Bact.* 17: 89–103.

(59) LIESKE, R. 1921 Morphologie und Biologie der Strahlenpilze, p. 130.

(60) LÖDE, A. 1903 Experimentale Untersuchungen über Bakterienantagonismus. *Centbl. Bakt.* [I] *Orig.*, 33: 196–208.

(61) LUCK, M. J., SHEETS, G., AND THOMAS, J. O. 1931 The rôle of bacteria in the nutrition of protozoa. *Quart. Rev. Biol.* 6: 46–58.

(62) LUTZ, O. 1909 Über den Einflusz gebrauchter Nährlösungem auf Keimung und Entwicklung einiger Schimmelpilze. *Ann. Mycol.* 7: 91–133.

(63) MACHACEK, J. E. 1928 Studies on the association of certain phytopathogens. *Macdonald Col. McGill Univ. Tech. Bul.* 7.

(63a) MCCORMACK, R. B. 1936 The associative action of some species of actinomyces. Thesis, Cornell University.

(64) MEIKLEJOHN, J. 1930, 1932 The effect of Colpidium on ammonia production by soil bacteria. *Ann. Appl. Biol.* 17: 614–637 (1930); 19: 584–608 (1932).

(65) MELIN, E. 1933, 1934 Zur Frage des Antagonisms zwischen freilebenden Mikroorganismen. Untersuchungen an Holzschliff. *Arch. Mikrobiol.* 4: 509–513 (1933); *Svensk. Skogsv. Tidskr.* 3–4: 397–616 (1934).

(66) MILLARD, W. A., AND TAYLOR, G. B. 1927 Antagonism of microorganisms as the controlling factor in the inhibition of scab by green manuring. *Ann. Appl. Biol.* 14: 202–216.

(67) MORITZ, O. 1932 Weitere Studien über die Ophiobolose des Wiezens. *Arb. Biol. Reichsanst. Land. Forstw.* 20: 27–48.

(68) NADSON, G. A. 1922 Bacterial and fungus pigments as means of defense and attack. *Bul. Jard. Bot. Repub. Russe. Sup.* 1:21:13–18.

(69) NADSON, G. A., AND ZOLKIEWICZ, A. I. 1922 *Spicaria purpurogenes* n. sp. Concerning the question of microbial antagonism. *Bul. Jard. Bot. Repub. Russe. Sup.* 1:21:1–12.

(70) NASIR, S. A. 1923 Some preliminary investigations on the relationship of protozoa to soil fertility, with special reference to nitrogen fixation. *Ann. Appl. Biol.* 10: 122–133.

(71) NENCKI, M. 1892 Über Mischkulturen. *Centbl. Bakt.* 11: 225–228.

(72) NICOL, H. 1934 Microbes in association. *Sci. Prog.* [London] 29: 236–243.

(73) NIKITINSKY, J. 1904 Über die Beeinflussung der Entwicklung einiger Schimmelpilze durch ihre Stoffwechselprodukte. *Jahrb. Wiss. Bot.* 40: 1–93.

(74) NOVY, F. G., ROEHM, H. R., SOULE, M. H., AND NOVY, JR., F. G. 1925 Microbic respiration. *Jour. Infect. Diseases* 36: 109–167, 168–232, 245–308, 343–382.

(75) OKUNUKI, K. 1931 Über die Beeinflussung des Wachstums der Schimmelpilze durch die von Rosahefen gebildeten Stoffe. *Japan. Jour. Bot.* 5: 401–455.

(76) PALEY, T., AND OSICHEVA, P. 1936 Reciprocal action of *Aspergillus niger* and *Penicillium luteum purpurogenum* Thom and Church. *Trudi Nauchno-Izslied. Inst. Pischtch. Promish.* 3(4): 146–156.

(77) PASTEUR, L. 1863 Nouvel exemple de fermentation déterminée par des animalcules infusoires pouvant vivre sans gas oxygene libre, et en dehors de tout contact avec l'air de l'atmosphère. *Compt. Rend. Acad. Sci.* [Paris] 56: 416–421.

(78) PHILPOT, C. H. 1928 Growth of Paramecium in pure cultures of pathogenic bacteria and in the presence of soluble products of such bacteria. *Jour. Morph.* 46: 85–129.

(79) PINOY, E. 1907 Role des bactéries dans le developpement de certaines Myxomycètes. *Ann. Inst. Pasteur* 21: 622–656, 686–700.

(80) PORTER, C. L. 1924, 1932 Concerning the characters of certain fungi as exhibited by their growth in the presence of other fungi. *Amer. Jour. Bot.* 11: 168–188 (1924); *Proc. Ind. Acad. Sci.* 41: 149–152 (1932).

(81) PRATT, C. A. 1924 The staling of fungal cultures. I. General and chemical investigation of staling by Fusarium. *Ann. Bot.* 38: 563–594, 599–615.

(82) PRINGSHEIM, E. G. 1920 Über die gegenseitige Schädigung und Förderung von Bakterien. *Centbl. Bakt.* [II] 51: 72–85.

(83) PULKKI, L. H. 1935 Production of bacterial growth stimulants by yeasts. *Ann. Acad. Sci. Fenn* A41: No. 1.

(84) PURDY, W. C., AND BUTTERFIELD, C. T. 1918, 1931 The effect of plankton animals upon bacterial death rates. *Amer. Jour. Pub. Health* 8: 499 (1918); *Indus. and Engin. Chem.* 23: 213–218 (1931).

(85) RAHN, O. 1906 Ueber den Einflusz der Stoffwechselprodukte auf das Wachstum der Bakterien. *Centbl. Bakt.* [II] 16: 417–429, 609–617.

(86) RAULIN, J. 1869 Études chimiques sur la végétation. *Ann. Sci. Nat., Bot.* (5) 11: 93–299.

(87) REGNIER, J., AND LAMBIN, S. 1934 Étude d'un cas d'antagonisme microbien. *Compt. Rend. Acad. Sci.* [Paris] 199: 1682–1684.

(88) REID, R. D. 1935 Some properties of a bacterial-inhibitory substance produced by a mold. *Jour. Bact.* 29: 215–220.

(89) REINHARDT, M. O. 1892 Das Wachstum der Pilzhyphen. *Jahrb. Wiss. Bot.* 23: 479–563.

(90) REMLINGER, P., AND NOURI, O. 1908 Les géloses dites vaccinées. *Compt. rend. Soc. Biol.* [Paris] 65: 364.

(91) ROSEN, H. R., AND SHAW, L. 1929 Studies on *Sclerotium Rolfsii*, with special reference to the metabolic interchange between soil inhabitants. *Jour. Agr. Res.* 39: 41–61.

(92) RUSSELL, E. J., AND HUTCHINSON, H. B. 1909, 1913 The effect of partial sterilization of soil on the production of plant food. *Jour. Agr. Sci.* 3: 111–144 (1909); 5: 152–221 (1913).

(93) SANFORD, G. B. 1926 Some factors affecting the pathogenicity of *Actinomyces scabies*. *Phytopath.* 16: 525–547.

(94) SANFORD, G. B., AND BROADFOOT, W. C. 1931 Studies of the effects of other soil-inhabiting microorganisms on the virulence of *Ophiobolus graminis* Sacch. *Sci. Agr.* 11: 512–528.

(95) SAVASTANO, G., AND FAWCETT, H. S. 1929 A study of decay in citrus fruits produced by inoculations with known mixtures of fungi at different constant temperatures. *Jour. Agr. Res.* 39: 163–198.

(96) STOKVIS, C. S., AND SMELLENGREBEL, N. H. 1911 Purification of water by infusoria. *Jour. Hyg.* 11: 481–486.

(97) TIMS, E. C. 1932 An actinomycete antagonistic to a Pythium root parasite of sugar cane. *Phytopath.* 22: 27.

(98) VASUDEVA, R. S. 1930 Studies in the physiology of parasitism. XII. On the effect of one organism in reducing the parasitic activity of another. *Ann. Bot.* 44: 557–564.

(99) WAKSMAN, S. A., AND HOTCHKISS, M. 1937 Viability of bacteria in sea water. *Jour. Bact.* To be published.

(100) WAKSMAN, S. A., AND STARKEY, R. L. 1923 Partial sterilization of soil, microbiological activities and soil fertility. *Soil Sci.* 16: 137–157, 247–268, 343–358.

(101) WARD, H. M. 1899 Symbiosis. *Ann. Bot.* 13: 549–562.

(102) WEHMER, C. 1893 Beiträge zur Kenntnis einheimlicher Pilze. Hannover and Leipzig.

(102a) WEINDLING, R. 1932, 1934, 1936 *Trichoderma lignorum* as a parasite of other soil fungi. *Phytopath.* 22: 837–845 (1932); 24: 1153–1179 (1934); 26: 1068–1070 (1936).

(103) WEINDLING, R., AND FAWCETT, H. S. 1936 Experiments in the control of Rhizoctonia damping-off of citrus seedlings. *Hilgardia* 10: 1–16.

(104) WIEBOLS, G. L. W., AND WIERINGA, K. T. 1936 Bacteriophagie een algemeen voorkomend verschijnsel. H. Veenman, Wageningen.

(105) WOLF, J. E. 1920 Beiträge zur Biologie des Pfeifferschen Influenzabazillus. Mischkulturen-Mischinfektion. *Centbl. Bakt.* [*I*] *Orig.* 84: 241–255.

(106) ZELLER, S. M., AND SCHMITZ, H. 1919 Studies in the physiology of fungi. VIII. Mixed cultures. *Ann. Missouri Bot. Gard.* 6: 183–192.

(107) ZOBELL, C. E. 1936 Bactericidal action of sea water. *Proc. Soc. Exp. Biol. and Med.* 34: 113–116.

ASSOCIATIVE AND ANTAGONISTIC EFFECTS OF MICROORGANISMS: II. ANTAGONISTIC EFFECTS OF MICROORGANISMS GROWN ON ARTIFICIAL SUBSTRATES[1]

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EXPERIMENTAL

Out of large numbers of organisms which make up the complex microbiological population of the soil, several were selected to be tested for their antagonistic action upon certain other organisms isolated from the soil and kept in laboratory culture. The antagonistic forms were selected to represent the three major groups of soil microorganisms; namely, fungi, actinomyces, and bacteria. The forms used most extensively were *Trichoderma lignorum*, isolated from a local soil; *Actinomyces* 3065, obtained from Professor Millard, who isolated it from peat land in Scotland; and *Bacterium fluorescens* also isolated from the soil and kept for several years in the culture collection.

The fungus *Trichoderma* was shown (1, 2) to have an antagonistic effect upon *Rhizoctonia* and other plant pathogenic fungi. In several preliminary studies carried out in this laboratory, this organism was found to repress the growth of a variety of soil fungi and bacteria, when grown together with them in solution cultures or in soil. This repressive effect was not due to exhaustion of nutrients or to an unfavorable effect of the reaction of the medium. The *Bact. fluorescens* was selected because it represents an extensive group of non-spore-forming soil bacteria and because it was also found, together with *B. pyocyaneum* and *Serratia marcescens*, to have a decided antagonistic effect upon other bacteria. The particular actinomyces was selected out of several which were tested for their ability to produce antagonistic effects upon other organisms; for this purpose, the anaxogramic method was used, and *Actinomyces* 3065 was selected because it was particularly effective.

The other organisms used in these investigations were either isolated from the soil or were taken from the culture collection. The antagonistic action of the three major organisms upon a common soil fungus and upon two soil actinomyces is brought out in table 1. Glucose-asparagine medium, consisting of 10 gm. glucose, 1 gm. asparagine, 0.5 gm. K_2HPO_4, 0.5 gm. $MgSO_4 \cdot 7H_2O$, 0.01 gm. $FeCl_3$, and 1000 cc. distilled water, was used. Seventy-five cubic centimeter portions of the medium were placed in 250-cc. flasks and sterilized

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by means of steam on 3 consecutive days. The test organisms were inoculated each into a group of flasks. After 2 and 7 days' incubation, at 28°C., the antagonistic forms were introduced. The results show that *Mycogone* was completely suppressed by *Bact. fluorescens* when the latter was inoculated

TABLE 1

Antagonistic effects of microorganisms

ORIGINAL ORGANISM	ORGANISM FOLLOWING	DAYS FOLLOWING	TOTAL INCUBATION, 18 DAYS		
			Nature of growth	Amount of growth, dry weight	Residual glucose
				mgm.	*mgm.*
Control	0	0	.....	...	674
Mycogone	0	0	Pure *Mycogone*	264	238
Mycogone	*Bact. fluorescens*	2	Growth of *Mycogone* arrested	38	0
Mycogone	*Bact. fluorescens*	7	Growth of *Mycogone* arrested	165	0
Mycogone	*Trichoderma*	2	*Mycogone* did not develop, typical *Trichoderma*	366	0
Mycogone	*Trichoderma*	7	Excellent *Mycogone* growth, little *Trichoderma*	350	0
Mycogone	*Actinomyces* 3065	2	Good *Mycogone* growth, slightly modified, some *Actinomyces* development	271	0
Mycogone	*Actinomyces* 3065	7	Normal *Mycogone*, limited *Actinomyces*	212	170
Actinomyces 3065	0	0	Good *Actinomyces* growth	94	120
Actinomyces 3065	*Trichoderma*	2	*Actinomyces* suppressed	215	0
Actinomyces 3065	*Trichoderma*	7	*Trichoderma* did not develop	89	0
Actinomyces 3065	*Bact. fluorescens*	2	*Actinomyces* suppressed	101	0
Actinomyces 3347	0	0	Good *Actinomyces* growth	120	280
Actinomyces 3347	*Bact. fluorescens*	2	*Actinomyces* suppressed	107	0
Actinomyces 3347	*Bact. fluorescens*	7	Limited *B. fluorescens* growth	128	0
Actinomyces 3347	*Trichoderma*	2	*Actinomyces* completely suppressed	265	0
Actinomyces 3347	*Trichoderma*	7	*Trichoderma* made no growth for 7 days, then began to grow suppressing the *Actinomyces*	166	249

2 or even 7 days after the *Mycogone*. *Trichoderma*, however, suppressed growth of *Mycogone* only when inoculated 2 days later; after 7 days, it had little effect upon the development of this fungus. The actinomyces did not modify to any large extent the growth of *Mycogone*, when inoculated either

after 2 or 7 days, although some inhibition was observed following the second inoculation, as shown by the reduction in amount of growth.

Actinomyces 3065 was completely suppressed by *Trichoderma* and by *B. fluorescens*, when these were inoculated 2 days after the actinomyces. When inoculated after 7 days, however, the *Trichoderma* did not grow at all, while the

TABLE 2

Antagonistic action of microorganisms in liquid media

ORIGINAL ORGANISM	SECONDARY ORGANISM	DAYS FOLLOWING	TOTAL INCUBATION, 16 DAYS			
			Nature of growth*	Amount of growth, dry weight	Nitrogen in growth	Residual glucose
				mgm.	*mgm.*	*mgm.*
Control	0	0	None	23†	0.5	840
Actinomyces 3065	0	0	A++++	101	7.6	0
Actinomyces 3065	*B. fluorescens*	2	A-0, B++++	100	8.6	0
Actinomyces 3065	*B. fluorescens*	4	A++, B+++	117	9.3	0
Actinomyces 3065	*B. fluorescens*	7	A+++, B+	110	8.4	0
Actinomyces 3065	*Trichoderma*	2	A-0, T+++	243	12.8	0
Actinomyces 3065	*Trichoderma*	4	A+++, T-0	97	7.2	0
Mycogone	0	0	M+++	299	14.9	62
Mycogone	*Actinomyces* 3065	2	M-0, A+++	104	8.0	0
Mycogone	*Actinomyces* 3065	4	M+++, A++	325	15.1	0
Mycogone	*Trichoderma*	2	M-0, T+++	343	15.1	0
Mycogone	*Trichoderma*	7	M+, T+++	363	9.3	0
Trichoderma	0	0	T++++	317	14.7	0
Trichoderma	*B. fluorescens*	1	T+++, B+++	230	11.8	0
Trichoderma	*B. fluorescens*	2	T+++, B+++	311	14.4	0
Trichoderma	*B. fluorescens*	4	T+++, B+++	339	14.6	0
Bact. fluorescens	*Trichoderma*	1	B+, T++	173	11.3	0
Bact. fluorescens	*Trichoderma*	2	B+, T+	138	10.1	0
Actinomyces 3347	0	0	A++++	72	5.7	94
Actinomyces 3347	*B. fluorescens*	4	A+, B++++	71	5.8	0
Actinomyces 3347	*B. fluorescens*	7	A+, B++++	94	6.9	21
Actinomyces 3347	*Trichoderma*	4	A-0, T++++ (yellow)	330	14.9	0
Actinomyces 3347	*Trichoderma*	7	A-0, T++++	333	14.9	13

* Growth: 0 = none, + trace, ++ moderate, +++ good, ++++ abundant. B = Bacterium, A = Actinomyces, M = Mycogone, T = Trichoderma.

† Largely phosphate precipitate.

B. fluorescens made only a very limited growth. *Actinomyces* 3347 was less antagonistic to *Trichoderma*, the growth of which was only somewhat delayed when inoculated 7 days after the actinomyces; the same was true of the action of this actinomyces upon the bacterium.

This experiment was repeated, using a greater variety of combinations between the antagonizing and antagonized organisms. A definite antagonistic

action of all three organisms was again obtained (table 2); the effect was different, however, with the different organisms. *Actinomyces* 3065 was completely suppressed by *Bact. fluorescens*, when the latter was inoculated after 2 days, but less so after 4 and very little after 7 days. The actinomyces was also suppressed by *Trichoderma*, after 2 days, but when allowed to grow for 4 days, the *Trichoderma* did not develop, in spite of the fact that there was still considerable sugar left at that period; the presence of sugar at the time of inoculation of the secondary organism has not been reported in the table. These results point definitely to the production of an antagonizing substance not only by *Trichoderma* towards the *Actinomyces*, but also by the latter against the former. *Mycogone* was repressed by the *Actinomyces* when inoculated 2 days after the fungus. When the actinomyces was added 4 days after the *Mycogone*, however, the growth of the latter was not repressed, while the former also made good growth, pointing to the fact that this fungus exerted little inhibition against the actinomyces. The same was true of the influence of *Trichoderma* upon *Mycogone*, the latter being repressed somewhat more completely.

The growth of *Trichoderma* was only slightly modified by the addition of *Bact. fluorescens*. The two organisms seemed to grow normally side by side; only when the bacterium was inoculated 24 days after the fungus, was there any slight suppression of the latter, which may possibly be due to the active competition for the nutrients. The growth of *Bact. fluorescens* was not suppressed by any of the several organisms tested, except by the *Trichoderma*; only the results of this combination are, therefore, reported in the table. *Actinomyces* 3347, which was previously found to be less actively antagonistic than 3065 was repressed readily both by *Bact. fluorescens* and by *Trichoderma*, even if the latter followed 7 days after the actinomyces. This confirms the previous observations of the lower antagonistic effect of *Actinomyces* 3347. The only evidence of any antagonistic action by 3347 was that *Trichoderma*, inoculated 4 days after the actinomyces, was colored yellow instead of its normal deep green; this always points to an abnormal growth of the *Trichoderma*.

In the subsequent experiment, a study was made of the antagonistic action of *Actinomyces* 3065, at different stages of its development, upon the growth of different fungi and bacteria. The asparagine-glucose medium was used; a number of 250-cc. Erlenmeyer flasks containing 50-cc. portions of this medium were inoculated simultaneously from young agar slant cultures of the actinomyces. All the flasks were placed in the thermostat, at 28°C. After 2, 4, and 7 days' incubation, a group of flasks was removed, inoculated with the secondary organism grown on agar slants, and again incubated. At the end of 16 days, dating from the original actinomyces inoculation, all the flasks were removed and analyzed. The amount of growth was determined, as in the previous experiments, by filtering the culture through weighed filter paper, washing with distilled water, and drying; the dried residue was weighed and

analyzed for total nitrogen. Because of this procedure the amount of bacterial growth was not included. The results are presented in table 3.

The growth of *Serratia* was not affected by the young actinomyces growth, namely after 2 and 4 days. After 7 days, however, *Serratia* suffered a decided injurious effect. The bacterium, when introduced 2 days after the actinomyces, practically suppressed the development of the latter. The *B. fluorescens* did not repress in any way the development of the actinomyces and was

TABLE 3

Antagonistic effect of Actinomyces *3065 upon other organisms*

SECONDARY ORGANISM	DAYS FOLLOWING THE *Actinomyces*	TOTAL INCUBATION, 16 DAYS			
		Nature of growth*	Amount of growth, dry weight	Nitrogen in growth	Residual glucose
			mgm.	*mgm.*	*mgm.*
Control	0	0	0	0	466.4
Actinomyces control	...	A++++	27	3.8	1.1
Serratia control†	...	B++++	..	...	140.0
Serratia	2	A+, B++++	29	3.6	314.8
Serratia	4	A++, B++++	40	4.5	19.5
Serratia	7	A++, B++	37	4.1	19.5
B. fluorescens	4	A++++, B++++	41	4.3	None
B. fluorescens	7	A++++, B++++	41	5.2	None
B. cereus	2	A++, B++	17	3.7	99.5
Trichoderma	2	A++, T+++	146	7.6	None
Trichoderma	4	A++++, T+	43	3.8	None
Trichoderma	7	A++++, T+	31	4.0	None
Mycogone	2	A++++, M+	50	6.5	1.7
Mycogone	4	A++++, M+	44	5.1	None
Mycogone	7	A++++, M+	22	2.8	None
Rhizopus MX	4	A++++, R-0	39	5.1	None
Rhizopus MX	7	A+, R++++	90	5.6	None
Botrytis control†	...	Bt+	39	2.0	380.8
Botrytis	2	A++, Bt+	18	3.2	None

* Growth: 0 = none, + trace, ++ moderate, +++ good, ++++ abundant. B = Bacterium, A = Actinomyces, T = Trichoderma, M = Mycogone, R = Rhizopus, Bt = Botrytis.

† No actinomyces.

not injured itself in any appreciable manner. *B. cereus*, however, seemed to have a decided injurious effect upon the actinomyces.

The effect of the actinomyces on the *Trichoderma* was similar to that found in previous experiments. At an early stage of the actinomyces development, the fungus was not greatly injured; it developed rapidly and gradually suppressed the actinomyces. In the older cultures of the actinomyces, *Trichoderma* developed only to a very limited extent, making a yellowish growth, which is characteristic of the abnormal development of this organism. *Myco-*

gone made a limited growth only in the very young actinomyces cultures; in older cultures, it did not grow at all or only in mere traces. The effect of

TABLE 4

Antagonistic action of Actinomyces *3065 at different stages of growth*

AGE OF ACTINOMYCES CULTURE	SECONDARY ORGANISM	INCUBATION AFTER SECONDARY INOCULATION	NATURE OF GROWTH*	AMOUNT OF GROWTH, DRY WEIGHT	NITROGEN IN GROWTH	GLUCOSE		pH
						Left	Consumed	
days		*days*		*mgm.*	*mgm.*	*mgm.*	*mgm.*	
0†	None	16	0	0	0	473	0	7.1
3	*Actinomyces* 3065	0	A+	22	3.3	462	11	8.0
3	*Actinomyces* 3065	3	A++	37	4.3	341	121	7.8
3	*Actinomyces* 3065	7	A++++	39	3.3	0	462	8.2
6	*Actinomyces* 3065	0	A+++	51	4.3	274	199	7.1
6	*Actinomyces* 3065	3	A++++	70	5.2	154	120	6.8
6	*Actinomyces* 3065	7	A++++	44	2.4	0	274	8.4
9	*Actinomyces* 3065	0	A++++	45	4.9	296	177	6.9
9	*Actinomyces* 3065	3	A++++	61	5.0	0	296	7.8
9	*Actinomyces* 3065	7	A++++	32	2.5	0	296	8.2
0	*Trichoderma*	3	T++++	122	5.6	246	227	5.6
0	*Trichoderma*	7	T++++	59	6.5	0	473	6.9
3	*Trichoderma*	3	A++, T-0	42	3.4	364	98	7.6
3	*Trichoderma*	7	A++, T+‡	77	5.8	30	432	6.7
6	*Trichoderma*	3	A++, T+‡	53	4.4	116	158	6.9
6	*Trichoderma*	7	A++, T+‡	74	4.4	20	254	7.2
9	*Trichoderma*	3	A++++, T+‡	60	4.8	153	143	6.9
9	*Trichoderma*	7	A++++, T-0	30	4.4	0	296	7.7
0	*Serratia*	3	B+++	...	...	129	344	4.6
0	*Serratia*	7	B+++	...	...	233	240	4.0
3	*Serratia*	3	A+, B+++	22	3.6	217	245	4.2
3	*Serratia*	7	A+, B+++	24	3.0	229	233	4.1
6	*Serratia*	3	A+, B+	47	5.0	37	237	5.7
6	*Serratia*	7	A++, B+	42	3.4	77	197	6.1
9	*Serratia*	3	A++++, B++	41	4.4	31	265	4.9
9	*Serratia*	7	A++, B+++	38	3.8	41	255	5.4
0	*Rhizopus*	3	R++++	117	6.0	5	468	3.5
0	*Rhizopus*	7	R++++	113	6.6	0	473	3.5
3	*Rhizopus*	3	A+, R++++	110	6.6	25	437	3.6
3	*Rhizopus*	7	A+, R++++	93	5.0	0	462	3.5
6	*Rhizopus*	3	A++, R++	83	4.8	34	240	3.6
6	*Rhizopus*	7	A++, R++	74	4.7	0	274	5.5
9	*Rhizopus*	3	A++++, R+	74	5.1	51	245	5.2
9	*Rhizopus*	7	A++++, R+	54	4.3	0	296	5.6

* Growth: 0 = none, + trace, ++ moderate, +++ good, ++++ abundant.

† 0 = no actinomyces.

‡ Trichoderma growth yellow.

the actinomyces upon the other two fungi was inconclusive, because of the limited number of observations.

A detailed study of the influence of *Actinomyces* 3065 upon the carbohydrate utilization and growth of different organisms is presented further in table 4. The media and the methods of culture and of analysis were similar to those used in the previous experiment. Here as well, the previous growth of the actinomyces either prevented completely the development of *Trichoderma* or resulted in limited yellowish growth, a sign of abnormal development. The *Serratia*, on the other hand, suppressed the growth of the actinomyces at an early stage of the development of the latter. *Rhizopus* grew well in the young cultures of the actinomyces, but made only a limited growth in older cultures. Because of the abundant lactic acid production by *Rhizopus*, which resulted in a decrease in the pH of the medium, the suppression of the actinomyces, when followed at an early stage of its development by *Rhizopus*, may be due to increased acidity to which the actinomyces are highly sensitive.

The change in reaction as a result of the development of the different organisms is of interest. The actinomyces brought about an increase in pH value or an increase in alkalinity, especially after all the sugar has been consumed.

TABLE 5

Influence of filtrate of Actinomyces *3065 upon the growth of different microorganisms*

ORGANISM	CONTROL		*Actinomyces* 3065		*Actinomyces* 3347		*Bact. fluorescens*		*Serratia*	
Age of filtrate.....*days*	4	10	4	10	4	10	4	10	4	10
Sugar left.....*mgm.*	435	268	0	25	320	242	205	143	209	176
Sugar consumed.....*mgm.*	...	...	435	243	115	26	230	125	226	92
Growth.....*mgm.*	0	0	47	43	15	11	...	...	...	...
pH.....	7.2	...	6.9	...	5.0	...	4.1	...	6.7	...

The growth of *Trichoderma* resulted in a slight decrease in pH value or an increased acidity, followed by a reversal to neutrality, after all the carbohydrate was consumed. The combination of the two organisms resulted in an intermediary reaction, depending on the extent of their development. *Serratia* produced extensive acidity in pure culture and in the 3-day-old actinomyces culture, in which the further growth of the latter was largely suppressed. The 6-day-old cultures of the actinomyces were least injured by the *Serratia*; this was also accompanied by the lowest acid production. The same is true of the effect of *Rhizopus*. However, when the *Rhizopus* was antagonized by the actinomyces, as in the 9-day-old cultures of the latter, the former grew little and produced little acidity.

These results bear out very emphatically the fact that different soil organisms can antagonize the growth of others, the degree of antagonism depending on the organism, the rapidity of its growth, and its specific metabolism. This antagonistic action can be measured by the appearance of the growth, its extent, and its metabolic products. In some cases, the antagonizing action was due to acid production, as was no doubt the case of *Rhizopus* and possibly of *Serratia*; in other cases, however, as with *Actinomyces* 3065 and *Trichoderma*,

the injurious effect was not due to an unfavorable change in reaction nor to the consumption of the nutrients.

In order to throw some light upon the nature and behavior of the specific antagonistic substance, *Actinomyces* 3065 was grown in glucose-asparagine medium for varying lengths of time. The cultures were filtered through a Seitz-filter into sterile flasks, and these were inoculated with various other organisms, after it had been ascertained that there were sufficient carbohydrate and available nitrogen in the sterile filtrate. The results obtained brought out definitely the fact that the actinomyces produces a substance definitely antagonistic to various fungi, of which *Trichoderma* is a type, and to bacteria, such as *Serratia*. The substance found in the filtrate from the 7- to 18-day-old cultures was particularly active; at 7 days it was sufficient to inhibit completely the growth of *Trichoderma*.

Aeration of the filtered culture, even for 10 minutes, brought about a reduction in the toxic principle of the actinomyces; long exposure to air seemed to have a similar effect. Boiling of the filtrate also resulted in the destruction of the injurious substance.

A typical experiment on the influence of the filtrate from 4- and 10-day-old cultures of *Actinomyces* 3065 upon the growth of the same organism, of another actinomyces, and of two bacteria is shown in table 5. The original medium contained 466 mgm. glucose in 50 cc.; this was reduced to 435 mgm. after 4 days' growth and to 268 mgm. after 10 days. The secondary organisms were incubated, at 28°C., for 14 days. The results show that *Actinomyces* 3065 was not injured in the least by the products of its own metabolism. The growth of the other actinomyces (3347), however, was almost completely prevented by the filtrate from the 10-day-old culture. The two bacteria were also injuriously affected.

SUMMARY

Different soil organisms found among the fungi, actinomyces, and bacteria are capable of producing, when grown on synthetic media, substances which are antagonistic to the growth of other soil organisms.

A detailed study has been made of the antagonistic effect of one species of actinomyces upon a variety of fungi, bacteria, and other actinomyces. The inhibiting effect produced by this organism was shown not to be due to exhaustion of nutrients or to unfavorable changes in reaction, but was found to be specific in nature.

The maximum production of the antagonistic substance took place in the cultures of the actinomyces 7 to 18 days old. The substance was then gradually destroyed. Aeration and heat brought about rapid destruction of this substance.

REFERENCES

(1) ALLEN, M. C., AND HAENSELER, C. M. 1935 Antagonistic action of Trichoderma on Rhizoctonia and other soil fungi. *Phytopath.* 25: 244–252.

(2) WEINDLING, R., AND FAWCETT, H. S. 1936 Experiments in the control of Rhizoctonia damping-off of citrus seedlings. *Hilgardia*, 10: 1–16.

ASSOCIATIVE AND ANTAGONISTIC EFFECTS OF MICROORGANISMS: III. ASSOCIATIVE AND ANTAGONISTIC RELATIONSHIPS IN THE DECOMPOSITION OF PLANT RESIDUES[1]

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Our present knowledge of the decomposition of plant and animal residues in soils and in composts is largely based upon studies with mixed populations or with pure cultures. In most instances, no attempt was made to determine the rôle of the individual members of the population in the processes involved in the decomposition of the various organic chemical constituents and of the mutual interrelationships of the numerous microorganisms, making up the complex populations, active in the decomposition processes. The use of pure cultures was further limited largely to a study of the decomposition of purified organic constituents, especially proteins and carbohydrates. Those few investigations, which dealt with the decomposition of complex plant materials by individual organisms (9, 7), brought out the fact that these do not attack the complex materials as a whole but that certain individual chemical constituents are decomposed in preference to others and that different organisms vary considerably in this respect. It has been shown repeatedly (12) that the addition to the soil of organic residues varying in chemical composition stimulates the development of different groups of microorganisms, which are no doubt largely concerned with the decomposition of the major constituents of these residues.

Different investigators, who have attempted to apply the results of pure culture studies to the activities of a mixed microbial population in soils and in composts, recognized the fact that some of the organisms used extensively in pure culture studies may not play the same function in nature as one might be tempted to generalize on the basis of the results thus obtained. This was found to hold true, for example, in the case of formation of ammonia from proteins by spore-forming bacteria. Conn (1) emphasized the care necessary in interpreting these results in terms of activities of the soil population as a whole. Winogradsky (13) went a step further, stating that most of the micro-

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organisms used in the study of decomposition of plant and animal residues were only "hot-house varieties," and, therefore, the results obtained in these investigations have no bearing whatsoever upon the complex soil processes; they may contribute to general microbiology but not to soil microbiology in a true sense.

In order to emphasize the possible confusion that may arise from the interpretations of pure culture studies, it is sufficient to cite the following illustrations: The presence of available carbohydrates in protein-containing bacteriological media was found to repress ammonia formation by various bacteria grown in pure culture in these media. This was due to the fact that certain bacteria are able to utilize the carbohydrate as a source of energy in preference to the protein; the protein will, therefore, be decomposed only to a limited extent and, since ammonia is primarily a waste product of energy utilization from proteins, no ammonia, or very little of it, will accumulate in the presence of an excess of the carbohydrate. This seemingly simple and obvious relationship brought forth, however, such vague generalizations as "fermentation in preference to putrefaction" (3). Aside from the complete lack of justification for the indiscriminate use of the terms "fermentation" and "putrefaction" to designate decomposition of carbohydrates and proteins, the statement itself was far from correct. Certain organisms, as in the case of various fungi, which are capable of utilizing as sources of energy and as nutrients both cellulose and proteins, will usually attack the latter in preference to the former. Further, even as simple and as readily an available carbohydrate as glucose can be neglected as a source of energy when proteins are present, in the case of certain organisms, namely, many actinomyces (2). A soil population, which contains all these organisms and many more, will bring about processes which are very distinct from those resulting from the activities of a single form grown in pure culture, especially on an artificial culture medium. This phenomenon is further complicated by the fact that microorganisms in a mixed population bring about numerous antagonistic and associative influences, as has been pointed out (10).

Without reviewing in detail the literature on the decomposition of complex plant substances by specific microorganisms, we may direct attention here only to several contributions which have a direct bearing upon the problem under consideration. Neller (4) has shown that when a mixture of *B. subtilis* and *B. vulgatus* was allowed to decompose cottonseed meal in soil, considerably more CO_2 (208 mgm.) was liberated than by either organism alone (136 mgm. and 168 mgm.); however, the amount of ammonia produced by the mixture of the two organisms was only slightly higher (10.7 mgm.) than that produced by either alone (10.6 mgm. and 8.2 mgm.). The same thing was true of the association of *B. mycoides* and *B. vulgatus;* the mixture of these bacteria liberated, in 12 days, 198.3 mgm. CO_2 and 7.7 mgm. ammonia, while the two organisms separately produced 41.6 mgm. and 168 mgm. CO_2 and accumulated 1.4 mgm. and 8.2 mgm. ammonia respectively. On the other hand, the association of

B. mycoides and *B. megatherium* produced less CO_2, but more ammonia, than either organism separately. A mixture of two fungi, namely, *Zygorhynchus* and *Trichoderma*, brought about the formation, from alfalfa meal in soil, of more CO_2 than was formed by the *Zygorhynchus* alone and less than that formed by the *Trichoderma* alone; however, a mixture of *Asp. niger* and *Trichoderma* produced more CO_2 than either organism alone. When the production of the two decomposition products is compared for the bacteria and fungi, it is found that the former liberated more ammonia in relation to the CO_2 than the latter.

Norman (5), using thermogenesis as a measure of microbial activities, found that microorganisms in mixtures had a depressing effect upon one another; a combination of two organisms gave a temperature rise nearer to that produced by the one having a lower thermogenic power. He came to the conclusion that the association may be either competitive or cooperative, as was also brought out by the results of Neller. Norman has further (6) shown that a mixed population brought about a greater decomposition of organic matter than one individual organism; this became particularly apparent when different temperatures were compared, since at each temperature there were organisms present in the mixture which were capable of bringing about extensive decomposition. Rege (7) found that certain fungi (*Coprinus*, *Aspergillus*) may be as active in the decomposition of plant residues as the total soil microflora; mixtures of fungi, however, brought about greater decomposition than pure cultures alone. Waksman (9) demonstrated that, in the decomposition of complex plant materials, different organisms are able to attack different constituents at varying rates; a mixture of *Trichoderma*, *Actinomyces*, and a bacterium decomposed only little more of the organic matter than the first organism alone, pointing to possible antagonistic effects among these organisms; a mixed soil flora decomposed much more of wheat straw than did the most active single organisms or the mixture of organisms tested; less nitrogen was assimilated by the total flora than by the individual organisms.

The fact that, in some cases, the mixed population was found to bring about no greater decomposition than individual microorganisms may have been due either to the absence of the specifically active forms in sufficient abundance or to the antagonistic effects of other forms present in the mixture.

EXPERIMENTAL

The following experiments were carried out primarily for the purpose of determining the specific functions of different groups of soil microorganisms in the decomposition of the various chemical constituents of plant materials and especially to obtain information concerning the mutualistic influences of these organisms. Three plant substances; namely, oat straw, corn stalks, and alfalfa, were used. A number of different organisms belonging to the fungi, actinomyces, and bacteria were compared, alone and in combination, with the mixed soil population. These organisms were selected on the basis of their specific physiological characteristics, their ability to attack certain definite

TABLE 1

Decomposition of alfalfa by pure and mixed cultures of microorganisms

On basis of dry material

INOCULUM	TOTAL PERIOD OF INCUBATION	TOTAL RESIDUE		WATER-SOLUBLE ORGANIC MATTER		HEMICELLULOSES		CELLULOSE		LIGNIN	TOTAL NITROGEN	WATER-SOLUBLE NITROGEN	NH_3-N
	days	*gm.*	*per cent loss*	*gm.*	*per cent loss*	*gm.*	*per cent loss*	*gm.*	*per cent loss*	*gm.*	*mgm.*	*mgm.*	*mgm.*
Control	39	9.120	....	2.090	....	0.760	....	2.060	....	1.170	284.5	58.8	5.1
Soil infusion	13	6.529	28.4	0.615	70.6	0.449	40.9	1.013	50.8	.....	265.1	54.6	21.3
Rhizopus	39	8.241	9.6	1.752	16.1	0.663	12.8	2.000	2.9	1.073	250.0	115.5	52.5
Rhizopus → *Trichoderma*	13 + 26	7.870	13.7	1.860	11.0	0.589	22.6	1.842	10.6	1.020	244.6	124.1	62.9
Rhizopus → *Trichoderma* → Soil infusion	13 + 13 + 13	5.668	37.8	0.762	63.5	0.362	52.4	0.969	53.0	0.989	199.0	75.6	22.5
Trichoderma	39	8.270	9.3	2.250	+7.7	0.724	4.7	2.079	0	1.041	271.3	163.5	60.9
Trichoderma → *Rhizopus*	13 + 26	8.120	11.0	2.181	+4.4	0.694	8.7	1.935	6.1	1.003	267.0	156.5	56.6
Trichoderma → *Rhizopus* → Soil infusion	13 + 13 + 13	5.445	40.3	1.077	48.5	0.352	53.7	0.935	54.6	0.930	214.3	91.8	27.9
Trichoderma → *Cunninghamella*	13 + 26	7.753	15.0	1.809	13.4	0.643	15.4	1.943	5.7	1.016	235.5	127.8	46.8
Trichoderma → *Bact. fluorescens*	13 + 26	8.166	10.5	1.753	16.1	0.650	14.5	1.928	6.4	1.115	221.1	107.4	32.1
Trichoderma → *Actinomyces* 3065	13 + 26	7.983	12.5	2.190	+4.8	0.649	14.6	1.962	4.8	1.023	260.9	152.4	56.4
Actinomyces 3065	39	7.608	16.6	2.169	+3.8	0.433	43.0	1.582	23.2	0.942	272.9	132.6	51.6
Actinomyces 3065	74	6.570	28.0	1.401	33.0	0.508	33.2	1.538	25.3	0.906	187.6	97.5	31.5
Actinomyces → Soil infusion	53 + 21	5.064	44.5	0.834	60.0	0.384	49.5	0.925	55.1	0.821	154.2	80.4	30.9
Rhizopus + *Trichoderma* + *Actinomyces*	39	7.830	14.2	1.824	12.7	0.627	17.5	1.985	3.6	1.040	224.8	125.1	52.2
Rhizopus + *Trichoderma* + *Actinomyces* → *Soil* infusion	26 + 13	6.433	29.5	0.738	64.7	0.432	43.2	1.172	43.1	1.154	243.0	75.3	27.0

chemical complexes, and their probable function in the decomposition processes. Three of the organisms; namely, *Trichoderma*, *Humicola*, and an impure culture of *Spirochaeta cytophaga*, were capable of bringing about active decomposition of cellulose; *Rhizopus*, *Asp. niger*, and other fungi were selected because of their ability to decompose simple carbohydrates but not cellulose; *Actinomyces* 3065 was selected because it was shown (11) to have, in artificial media, specific antagonistic effects upon other organisms; several species of *Azotobacter* were also used because of their ability to fix atmospheric nitrogen.

The first experiment was carried out as follows: 10-gm. portions of the ground plant materials, in an air-dry condition, were placed in 250-cc. Erlenmeyer flasks and 30 cc. tap water added; the flasks were plugged with cotton and sterilized in flowing steam on three consecutive days. The flasks were divided into four lots and inoculated with several different organisms. After 12–13 days' incubation at 28°C., one flask was taken from each lot, well shaken, and left without further inoculation; the three other flasks were also shaken and inoculated with another organism; 12–13 days later, the last three flasks were again shaken, one was left uninoculated further, one was inoculated with a soil infusion, and one, with a third organism. All the flasks were then incubated again for certain periods of time at 28°C., as shown in the tables, and finally removed for analysis. A few of the flasks containing the different plant materials were left as controls, uninoculated, and a few were inoculated with three organisms simultaneously. The sequence of the organisms is indicated in the tables by arrow signs.

Decomposition of alfalfa. Alfalfa represents a well-balanced medium for microbial development, primarily because of its high organic nitrogen and mineral content. The results presented in table 1 show that the growth of the fungus *Rhizopus* upon alfalfa resulted in the destruction of only about 10 per cent of the dry matter in 39 days; this loss was largely at the expense of the water-soluble substances and the hemicelluloses. The proteins were also decomposed, as shown by the accumulation of water-soluble forms of nitrogen including ammonia. The cellulose was attacked only to a very limited extent, if at all. There was only a slight reduction in the lignin content. When, after 13 days of growth, *Rhizopus* was followed by *Trichoderma*, greater decomposition took place. The increased decomposition was largely at the expense of the cellulose and also of the hemicelluloses and proteins. When these two fungi were followed, 26 days after the first inoculation, by an infusion of fresh soil, the decomposition process was greatly increased and resulted in a loss of about 38 per cent of the dry material, at the end of the total 39-day incubation period. Some of the chemical constituents of the alfalfa were decomposed to a greater extent than the total material, as shown by a loss of 63.5 per cent water-soluble substances, 52.4 per cent hemicelluloses, and 53 per cent cellulose. There was less ammonia found in the residue with the mixed population following the fungi than that with the fungi alone; this was due to greater

synthesis of microbial cell substance and to a greater loss of nitrogen, as shown by a marked reduction in the total residual nitrogen. When the changes brought about by the soil infusion following the two fungi are compared with the decomposition of the alfalfa by the infusion alone, it becomes evident that the growth of the fungi previous to the mixed microbial population resulted in a marked influence upon the rate and nature of the decomposition processes. The difference was especially striking in regard to the nitrogen losses: the soil infusion alone brought about only an insignificant loss of nitrogen; the growth of the fungi, followed by the soil infusion, resulted in a loss of nearly 30 per cent of the total nitrogen.

Trichoderma alone brought about the same amount of total decomposition of the alfalfa as did the *Rhizopus*. It acted, in pure culture, primarily upon the proteins, as shown by the extensive transformation of the total nitrogen into soluble forms. The water-soluble constituents of the alfalfa, however, were not attacked at all, since their concentration was increased at the expense of the insoluble nitrogenous substances. When *Trichoderma* was followed, after 13 days of growth, by *Rhizopus;* the latter grew only to a very limited extent, as could be demonstrated both by macroscopic and microscopic examination of the material; this was accompanied by only a slight increase in the decomposition of the alfalfa.

It is of special interest to note in connection with the decomposition of alfalfa by these two fungi, that *Trichoderma*, a strong cellulose-decomposing organism, did not attack, in pure culture, the cellulose of the alfalfa; however, when followed by *Rhizopus*, a non-cellulose-decomposing organism, and especially when preceded by it, it decomposed a certain amount of cellulose. The answer to this peculiar relationship is probably to be looked for in the decomposition of the protein, which was vigorously attacked by *Trichoderma*. Of a total 284.5 mgm. nitrogen as protein in the original alfalfa, only 58.8 mgm., or about 20 per cent, was in a water-soluble state; the *Trichoderma* without the *Rhizopus*, transformed 163.5 mgm., or over 57 per cent, of the total nitrogen into water-soluble forms, 156.5 mgm. when followed by the *Rhizopus*, and only 124 mgm. when preceded by the latter organism. This extensive transformation of the nitrogenous compounds by the two fungi accounts for the increase in water-soluble material and for the transformation of over 20 per cent of the nitrogen into ammonia. In view of the fact that *Rhizopus* attacks readily the nitrogenous compounds of alfalfa, its presence brought about a state of competition for the available protein between the two fungi, with the result that the *Trichoderma* was forced to obtain some of its energy from the cellulose.

When *Trichoderma* was followed by *Cunninghamella* or by *Bact. fluorescens*, the effect was similar to that of the *Rhizopus*. The explanation suggested here, therefore, is that *Trichoderma* prefers proteins as sources of energy to cellulose; when it is accompanied, however, by other organisms, which are unable to attack cellulose but which are capable of decomposing proteins, *Trichoderma*

will decompose the cellulose. When the mixed soil population followed the growth of *Trichoderma* and *Rhizopus* on the alfalfa, the changes in the chemical constituents were practically the same as when the order of the two fungi was reversed, except that the loss of nitrogen was somewhat less.

The actinomyces alone grew vigorously on the alfalfa, bringing about far greater decomposition than did the fungi, either alone or in association. When an incubation period of 39 days was used, the organism attacked the hemicelluloses, cellulose, and proteins, which led to an increase in water-soluble material and an accumulation of ammonia; on further decomposition, the water-soluble substances were also utilized and a large part of the nitrogen was lost. When the actinomyces was followed by the mixed soil population, still greater decomposition took place, to the extent of 44.5 per cent of the total dry matter in the alfalfa; this was accompanied by extensive losses of nitrogen, namely, 46 per cent of the total nitrogen present, in 74 days. When following *Trichoderma*, however, the actinomyces did not bring about any greater decomposition of the material than did any of the fungi, because it was antagonized in its development by the latter.

The two fungi and the actinomyces inoculated simultaneously attacked the alfalfa to about the same extent as the mixture of the two fungi alone, especially when *Rhizopus* was followed by *Trichoderma*. When the mixture of these organisms was followed by soil infusion, the total effect on the alfalfa was no greater, but even less, than in the case of the two fungi alone. The effect of the three organisms, as far as assisting the soil population, reduced itself to nil, since the total decomposition was about on a par with that brought about by the soil infusion alone.

In general, the mixed soil population brought about the most extensive decomposition of the alfalfa, especially when following the fungi and actinomyces. Numerous heterotrophic bacteria present in the infusion were able to attack the water-soluble substances, as shown by the extensive destruction of the latter. This seemed to favor particularly the development of the cellulose- and hemicellulose-decomposing organisms. The decomposition of the carbohydrates was accompanied by the conversion of some of the soluble nitrogenous substances into insoluble forms, as shown by the limited concentration of ammonia.

The results of the decomposition of lignin in the alfalfa are somewhat difficult to interpret. The high protein concentration renders an exact determination of the lignin somewhat open to criticism. Little significance can, therefore, be attached to a reduction of about 10 per cent in the lignin content. The only definite evidence of lignin destruction is found in the case of the actinomyces, especially when this organism was followed by a mixed soil population. To what extent this destruction of the lignin is a cause of, or associated with, the losses of nitrogen is still to be determined.

Decomposition of corn stalks. Corn stalks were found, in preliminary experiments, to be more resistant to decomposition than alfalfa and oat straw, hence

TABLE 2

Decomposition of corn stalks by pure and mixed cultures of microorganisms

COMBINATION OF ORGANISMS	PERIOD OF INCUBATION	TOTAL RESIDUE		WATER-SOLUBLE ORGANIC MATTER		HEMICELLULOSES		CELLULOSE		LIGNIN
	days	*gm.*	*per cent loss*	*gm.*	*per cent loss*	*gm.*	*per cent loss*	*gm.*	*per cent loss*	*gm.*
Control	67	9.060	....	1.101	....	1.859	....	2.590	....	1.201
Soil infusion	41	7.171	20.9	0.579	47.4	1.390	25.3	1.935	25.3	1.196
Rhizopus	67	8.151	10.0	0.657	40.3	1.540	17.2	2.610	0	1.189
Rhizopus → *Trichoderma*	13 + 54	7.998	11.7	0.483	56.1	1.437	22.7	2.452	5.4	1.212
Rhizopus → *Trichoderma* → Soil infusion	13 + 13 + 41	6.902	23.8	0.390	64.5	1.252	32.7	1.932	25.4	1.254
Rhizopus → *Trichoderma* → *Actinomyces*	13 + 13 + 41	7.469	17.8	0.558	49.3	1.308	29.7	2.383	8.0	1.180
*Trichoderma**	67	7.934	12.5	0.636	42.2	1.322	29.0	2.563	1.0	1.201
Trichoderma → *Rhizopus* → Soil infusion	13 + 13 + 41	7.350	18.9	0.408	62.9	1.282	31.1	2.365	8.7	1.198
Rhizoctonia	41	7.615	16.0	0.618	43.8	1.629	12.4	2.159	16.6	1.167
Asp. niger	41	8.586	5.3	0.480	56.4	1.746	6.1	2.629	0	1.208
Mycogone → *Trichoderma*	26 + 16	7.915	12.7	0.762	30.7	1.490	19.9	2.261	12.7	1.259
Cunninghamella + *Trichoderma*	53	7.846	13.4	0.615	44.1	1.339	28.0	2.470	4.6	1.122
Azotobacter† → *Trichoderma*	13† + 54	7.724	14.8	0.627	43.0	1.251	32.8	2.427	6.3	1.196
Azotobacter† → *Trichoderma* → Soil infusion	13† + 13 + 41	7.547	16.7	0.330	70.0	1.307	29.7	2.338	9.7	1.257
Rhizopus + *Trichoderma* + *Actinomyces*	67	7.065	22.0	0.594	46.0	1.063	42.9	2.282	11.9	1.121
Rhizopus + *Trichoderma* + *Actinomyces* → Soil infusion	26 + 41	6.547	27.7	0.387	64.8	1.076	42.2	1.945	24.9	1.110

* *Rhizopus* and *Actinomyces* following *Trichoderma* did not develop, and the analytic results were exactly the same as with *Trichoderma* alone, hence the results are not included.

† *Azotobacter* did not develop at all on the corn stalks, hence these cultures can be considered as mere delayed inoculations with *Trichoderma* and with soil infusion.

a longer period of incubation was employed in these experiments, namely, 67 days. The results reported in table 2 show that, during this period, *Rhizopus* decomposed only 10 per cent of the total plant material; the loss was largely at the expense of the water-soluble substances and the hemicelluloses. When this organism was followed by *Trichoderma*, the amount of decomposition was increased only to a limited extent, and the rate of decomposition of the different constituents was not changed appreciably, except for a small increase in the decomposition of hemicelluloses and for a limited decomposition of the cellulose. *Trichoderma* grew only at the very surface of the mass of plant material overgrown with the mycelium of the *Rhizopus*, and did not penetrate into the mass.

When *Trichoderma* was followed by *Actinomyces*, or was combined with the latter and with *Rhizopus*, decomposition of the corn stalks was greatly stimulated; the very nature of the process was changed, as shown by extensive decomposition of the cellulose and hemicelluloses. It is of special interest to note here that the *Actinomyces* alone made no growth at all on the corn stalks. Fresh lots of the material were inoculated several times with cultures of this organism, without any success in obtaining growth. However, when the inoculation with the *Actinomyces* was made after the two fungi grew upon the corn stalks, or simultaneously with the fungi, it made a very extensive growth and brought about considerable destruction of the corn stalk material. Just why the *Actinomyces* was unable to grow on the corn stalks and what the specific effect of the fungi was in rendering this medium favorable for its development still remain to be determined. It is possible that this plant residue contains substances injurious to the development of the particular actinomyces; possibly these substances are destroyed by the fungi. It may also be due to the formation or synthesis by the latter of complexes which can be utilized readily by the actinomyces. One finds here a striking illustration of associative action of different organisms in the breakdown of complex plant materials.

The complex soil population brought about considerable decomposition of the corn stalks, namely, 20.9 per cent of the total material; this was largely at the expense of the water-soluble substances, hemicelluloses, and cellulose. When the soil infusion followed the fungi, *Rhizopus* and *Trichoderma*, decomposition was even greater, namely, 23.8 per cent, and greatest when following these two fungi and *Actinomyces*, namely, 27.7 per cent of the total dry material. The increase in decomposition in the presence of these organisms was due to greater destruction of the water-soluble substances and hemicelluloses. When *Trichoderma* preceded *Rhizopus*, however, their combined activities resulted in depressing the decomposition of the corn stalks by the mixed soil population.

In the mixtures containing the actinomyces, the lignin in the stalks was also partly attacked. Just as in the case of the alfalfa, the destruction of the lignin seemed to be definitely associated with the presence of the actinomyces.

TABLE 3

Decomposition of oat straw by pure and mixed cultures of microorganisms

On basis of dry material

COMBINATION OF ORGANISMS	PERIOD OF INCUBATION	TOTAL RESIDUE		WATER-SOLUBLE ORGANIC MATTER		HEMICELLULOSES		CELLULOSE		LIGNIN
	days	*gm.*	*per cent loss*	*gm.*	*per cent loss*	*gm.*	*per cent loss*	*gm.*	*per cent loss*	*gm.*
Control	50	9.393	....	0.537	.....	2.084	....	3.290	....	1.465
Soil infusion	24	7.549	19.6	0.546	+1.3	1.412	32.2	2.437	27.1	1.298
Rhizopus	50	8.839	5.9	0.546	+1.3	1.811	13.1	3.217	2.3	1.462
Rhizopus → *Trichoderma*	13 + 37	7.895	16.0	0.617	+14.8	1.505	27.9	2.593	22.4	1.445
Rhizopus → *Trichoderma* → Soil infusion	13 + 13 + 24	7.879	16.1	0.540	+0.6	1.534	26.4	2.652	19.4	1.430
Trichoderma	50	8.194	12.8	0.582	+8.4	1.557	25.3	2.626	21.4	1.525
Trichoderma → *Rhizopus*	13 + 37	8.458	10.0	0.620	+15.5	1.618	22.4	2.738	16.7	1.553
Trichoderma → *Rhizopus* → Soil infusion	13 + 13 + 24	8.050	14.3	0.528	1.7	1.557	25.3	2.590	22.6	1.554
Azotobacter	50	9.222	1.8	0.372	30.7	2.144	+2.9	3.294	0	1.480
Azotobacter → *Trichoderma*	13 + 37	8.400	10.6	0.617	+14.8	1.615	22.6	2.741	16.7	1.567
Azotobacter → *Trichoderma* → Soil infusion	13 + 13 + 24	8.087	14.0	0.564	+5.0	1.568	24.8	2.734	16.9	1.568
Actinomyces 3065	50	8.522	9.3	0.597	+11.2	1.573	24.5	3.199	2.8	1.359
Actinomyces → *Trichoderma*	13 + 37	8.655	7.9	0.657	+22.3	1.586	23.9	3.139	4.6	1.458
Actinomyces → Soil infusion	18 + 24	6.883	26.7	0.444	17.3	1.240	40.5	2.413	26.7	1.232

Azotobacter, alone or in association with the fungi, did not grow on the corn stalks at all. *Asp. niger* attacked only the water-soluble substances in the stalks; the hemicelluloses were utilized to a limited extent, but not the cellulose. *Rhizoctonia* decomposed both the water-soluble substances and the cellulose; the hemicelluloses were attacked only to a limited extent, and possibly also the lignin. The *Cunninghamella*, a non-cellulose-decomposing organism, and *Mycogone* stimulated both the growth and cellulose decomposition by *Trichoderma*; otherwise, they did not increase to any large extent the amount of decomposition of the corn stalks by this organism.

It is of particular interest to note that a mixture of *Trichoderma*, *Rhizopus*, and *Actinomyces* brought about as much decomposition of the corn stalks as did the complex soil population; the former, however, attacked more of the hemicelluloses and less of the cellulose.

Decomposition of oat straw. Several significant results were obtained in the study of the decomposition of the third plant residue, namely, oat straw (table 3). The nitrogen-fixing organism *Azotobacter* grew readily upon this substrate. This growth was made entirely at the expense of the water-soluble substances; these accounted completely for the loss of the total material brought about by this organism. However, no nitrogen was fixed. The nitrogen present in the water-soluble material of the straw was sufficient to supply all the needs of the organism. This was further confirmed by the fact that, as a result of *Azotobacter* growth, there was a reduction of 3.0 mgm. in the water-soluble nitrogen of the straw (14.7 in control against 11.7 in the culture). The loss in the total water-soluble material was 165 mgm.; this served as a source of energy for the *Azotobacter*, which also converted the water-soluble nitrogen into cell proteins without fixing any atmospheric nitrogen. The addition of *Trichoderma* or of soil infusion to the cultures of *Azotobacter* did not hasten its development and, likewise, did not result in any fixation of nitrogen. This was especially significant since the oat straw represents a nitrogen-poor and carbohydrate-rich substrate, which should have made it an ideal substrate for nitrogen fixation. The fact that no atmospheric nitrogen was fixed shows that cellulose-rich material, even in the presence of cellulose-decomposing organisms, cannot supply the energy required by *Azotobacter*; it certainly did not under the conditions of these experiments.

Another characteristic property of the oat straw was the extensive growth of the *Actinomyces* upon this plant material. This resulted in the decomposition of a considerable part of the hemicelluloses, some cellulose, and possibly some lignin. When *Trichoderma* followed *Actinomyces*, less of the straw was decomposed than by either organism alone. This was no doubt due to the mutual antagonistic effects of the two organisms, as was shown in the studies of these organisms on artificial media (11). The organisms present in the mixed soil population were not antagonized by the actinomyces, but were rather stimulated, with the result that a greater amount of decomposition of the material was brought about, especially of the hemicelluloses and lignin.

Rhizopus decomposed less of the oat straw than of the other two plant materials, largely because of the low concentrations in the straw of the water-soluble substances, which this organism attacks by preference. This organism did not exert any antagonistic action upon the *Trichoderma*, since the combined growth of the two was greater than that of either alone, as was the amount of cellulose decomposed. However, the previous growth of *Trichoderma* exerted a decided antagonistic action upon the *Rhizopus*, as shown by reduced decomposition, and could easily be demonstrated by the macroscopic and microscopic appearance of the material.

TABLE 4

Influence of lime, nutrient salts, and associative organisms upon the growth of actinomyces on corn stalks

TREATMENT	ORGANISM	GROWTH OF *Actinomyces*	TOTAL DECOMPOSITION	DECOMPOSITION WATER-SOLUBLE ORGANIC MATTER	DECOMPOSITION OF HEMICELLULOSES	DECOMPOSITION OF CELLULOSE
			per cent	*per cent*	*per cent*	*per cent*
None	Control	None	0	0	0	0
None	*Actinomyces* 3065	Limited	1.0	4.6	0	2.7
None	*Humicola*	....	26.3	42.0	4	3.8
None	*Humicola* + *Actinomyces* 3065	Extensive	31.1	37.9	21.1	7.1
$CaCO_3$	*Actinomyces* 3065	Extensive	21.6	28.5	19.3	6.6
$CaCO_3$	*Actinomyces* 3018	Extensive	23.7	29.7	16.5	9.6
$CaCO_3$	*Actinomyces* 3310	Moderate	14.7	33.4	14.3	0
$CaCO_3$	*Actinomyces* 3065 + *B. fluorescens*	Extensive	24.2	35.3	22.6	7.1
$CaCO_3$	*Humicola*	....	25.1	43.5	9	12.0
$CaCO_3$	*Humicola* + *Actinomyces* 3065	Extensive	24.3	41.7	18.5	6.4
$NaNO_3$ + K_2HPO_4	*Humicola*	....	24.0	5.5	35.3	19.2
$NaNO_3$ + K_2HPO_4	*Actinomyces* 3065	Moderate	9.1	9.9	12.5	0
$NaNO_3$ + K_2HPO_4	*Humicola* + *Actinomyces* 3065	Moderate	28.9	13.0	33.2	17.1

The greatest amount of decomposition was brought about, in the case of the oat straw as well, by the mixed soil population. The previous growth of the fungi did not modify the amount and nature of the decomposition process, whereas the preceding growth of the *Actinomyces* did. The decomposition of the lignin was again definitely associated with the presence of the actinomyces.

Another interesting phenomenon in connection with the decomposition of the oat straw was the increase in water-soluble material. Only the *Azotobacter* brought about a reduction in this group of constituents; the same thing was true to a more limited extent of the soil infusion, especially when following the

Actinomyces. The fungi, however, seemed to attack by preference the water-insoluble organic constituents of the straw.

Influence of chemicals and associative organisms upon the decomposition of corn stalks by actinomyces. It was shown previously that corn stalks seem to contain substances which render it resistant to decomposition by the actinomyces. In order to throw light upon the specific nature of this phenomenon, a detailed experiment was carried out to test the effect of different organisms and chemicals in modifying the nature of this medium for their growth. In this experiment, the fungus *Humicola* was used largely as the associative organism. The nature of the medium was corrected by the addition of $CaCO_3$ (1 gm. per 10 gm. of material), as well as by a mixture of $NaNO_3$ and K_2HPO_4. Incubation took place, at 28°C., for 75 days.

The results (table 4) show that the actinomyces alone made very little growth upon the corn stalks; when preceded by *Humicola*, its growth was extensive; there was also greater decomposition of the material as a whole and especially of the complex carbohydrates. The resistance of the corn stalk material to the growth of different actinomyces could also be corrected by the addition of $CaCO_3$; under these conditions, the presence of *Humicola* or of *Bact. fluorescens* had only a limited effect in increasing decomposition of the material. The addition of nutrient salts ($NaNO_3$ and K_2HPO_4) corrected the unfavorable condition only to a limited extent. Under these conditions, the presence of *Humicola* had a highly favorable effect.

These results prove very emphatically that different organisms may produce decided favorable influences upon the growth of other organisms in a mixed population.

DISCUSSION

The complex microbiological population responsible for the decomposition of plant and animal residues in soils and in composts presents a variety of associative and antagonistic influences upon one another. The results of a study of the decomposition of several plant materials by different pure and mixed cultures of microörganisms amply illustrate the various relationships involved. Although, as a rule, the individual organisms did not bring about as extensive decomposition of the different plant materials as did the mixed soil population, they exerted considerable influence not only upon one another but also upon the population as a whole. Several of the more striking relationships only need be emphasized here.

A strong cellulose-decomposing fungus was found to attack the proteins of alfalfa plants in preference to the cellulose. However, in the presence of another organism, which could also attack the proteins but not the cellulose, the first organism was forced to attack the complex carbohydrate. It was also observed in other cases, as with corn stalks, that the presence of non-cellulose-decomposing fungi and bacteria stimulated cellulose decomposition

by organisms capable of doing so. This was probably also due to the fact that the former consumed the soluble and more readily available carbohydrates, thus forcing the latter to exert a property which they themselves did not possess.

Although the mixed soil population brought about quantitatively greater decomposition of the alfalfa than did the pure cultures of fungi and actinomyces, the nature of the decomposition process was considerably modified when the mixed population was preceded by these organisms. Of particular interest in this connection is the loss of nitrogen. This loss was found to take place particularly in the case of certain associations of microörganisms. The loss was extensive when the mixed soil population was preceded by certain fungi capable of attacking the proteins in preference to the carbohydrates; it was particularly marked in the case of decomposition of the alfalfa by actinomyces, and especially when the latter was followed by a mixed soil population.

Another striking instance of associative activities of microörganisms was found in the ability of the actinomyces to grow on corn stalks. The organisms tested refused to grow, in pure culture, upon this plant material. When preceded or accompanied by various fungi, however, it made excellent growth. This resistance of the corn stalks to actinomyces growth could be completely overcome by the addition of $CaCO_3$ but only partially by nutrient salts, namely, $NaNO_3$ and K_2HPO_4. It is of particular interest to note that when the unfavorable condition was corrected by the $CaCO_3$, the associative organisms no longer favored actinomyces development; however, when the condition was only partially corrected by the nutrient salts, the associative organisms again exerted a favorable effect. This points definitely to the fact that numerous associative influences are exerted in the case of a complex population.

The growth of the nitrogen-fixing *Azotobacter* was also found to present certain significant aspects of population growth. Of the various plant materials tested for the growth of this organism, only oat straw, especially certain chemical constituents of this material, was utilized. Under these conditions, the organism did not fix any nitrogen, since it was able to make use of those compounds of nitrogen already present among the water-soluble constituents of this plant material.

As to the decomposition of some of the resistant plant constituents, like the lignins, it was found that the presence of actinomyces in the mixture of organisms was definitely associated with this process.

These results, as well as the various other studies of associative and antagonistic effects of different organisms upon one another, not reported here, brought out the fact that, in connection with the processes of transformation of plant and animal residues in soils and in composts by a mixed population, numerous associative and antagonistic influences take place. As a result of this, the decomposition processes which are brought about by a complex population are quite distinct from those of a single organism in pure culture.

SUMMARY

A study has been made of the associative growth of different fungi, actinomyces, and bacteria upon different plant materials and of the resultant decomposition of the latter.

It was found that the presence of one organism may modify considerably the growth of another. The decomposition of alfalfa by a *Trichoderma* was modified considerably by the presence of various fungi and bacteria; these organisms, although by themselves unable to decompose cellulose, were capable of favoring the decomposition of the cellulose by *Trichoderma*.

Corn stalks could not be attacked by pure cultures of actinomyces. However, when certain fungi were previously grown upon this plant material, the growth of the actinomyces was greatly favored; this was accompanied by increased decomposition. The unfavorable condition could also be corrected by the addition of lime, and only partly by nitrate and phosphate.

Different fungi were found to vary considerably in their ability to attack the various chemical constituents of plant residues and to exert varying influences upon the activities of other organisms, as well as of the soil population as a whole.

Azotobacter was found capable of utilizing the carbohydrates of oat straw, but it did not fix any nitrogen. In the presence of cellulose-decomposing fungi, it also made good growth, but this process, as well, was not accompanied by nitrogen-fixation. The combined nitrogen of the straw was utilized by this organism for its synthetic needs.

Lignin decomposition took place only when actinomyces were present in the mixture of organisms.

REFERENCES

(1) CONN, H. J. 1916, 1917, 1923 Are spore-forming bacteria of any significance in soil under normal conditions? N. Y. Agr. Exp. Sta. Tech. Bul. 51 (1916); 58 (1917); 97 (1923).

(2) GUITTONNEAU, G. 1924 Sur la production de l'urée an cours de l'ammonification par les Microsiphonées. *Compt. Rend. Acad. Sci.* [Paris] 178: 1383–1385.

(3) KENDALL, A. J. 1916 Bacteriology, General, Pathological and Intestinal. Philadelphia.

(4) NELLER, J. R. 1918 Studies on the correlation between the production of carbon dioxide and the accumulation of ammonia by soil organisms. *Soil Sci.* 5: 225–239.

(5) NORMAN, A. G. 1930 The biological decomposition of plant materials. III. Physiological studies of some cellulose-decomposing fungi. *Ann. Appl. Biol.* 17: 575–613.

(6) NORMAN, A. G. 1931 The biological decomposition of plant materials. IV. The biochemical activities on straws of some cellulose-decomposing fungi. *Ann. Appl. Biol.* 18: 244–259.

(7) REGE, R. D. 1927 Bio-chemical decomposition of cellulosic materials, with special reference to the action of fungi. *Ann. Appl. Biol.* 14: 1–44.

(8) WAKSMAN, S. A. 1926 The origin and the nature of the soil organic matter or soil "humus": III. The nature of the substances contributing to the formation of humus. *Soil Sci.* 22: 323–333.

(9) WAKSMAN, S. A. 1931 Decomposition of the various chemical constituents of complex plant material by pure cultures of fungi and bacteria. *Arch. Microbiol.* 2: 136–154.

(10) WAKSMAN, S. A. 1937 Associative and antagonistic effects of microorganisms: I. Historical review of antagonistic relationships. *Soil Sci.* 43: 51–68.

(11) WAKSMAN, S. A., AND FOSTER, J. W. 1937 Associative and antagonistic effects of microorganisms: II. Antagonistic effects of microorganisms grown on artificial substrates. *Soil Sci.* 43: 69–76.

(12) WAKSMAN, S. A., AND STARKEY, R. L. 1924 Influence of organic matter upon the development of fungi, actinomycetes, and bacteria in the soil. *Soil Sci.* 17: 373–378.

(13) WINOGRADSKY, S. 1924 La méthode directe dans l'étude microbiologique du sol. *Chim. et Indus.* [Paris] 11: 1–8.

THE EFFECT OF CARBON DIOXIDE ON SOIL REACTION AND ON THE SOLUBILITY OF PHOSPHORUS IN SOILS[1]

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The more important factors affecting the availability of phosphorus in soils are the kind and amount of phosphates present, the reaction of the soil, the organic matter content, the silica-sesquioxide ratio, the exchange capacity, and the ionic concentration of the soil solution.

McGeorge and Breazeale (10) determined the solubility effect of carbon dioxide on the mineral phosphates vivianite, lazulite, wavellite, and dufrenite. They reported that carbon dioxide-saturated water increased the solubility of the vivianite to a measurable degree, whereas lazulite was not affected and wavellite and dufrenite were affected only slightly.

Breazeale and Burgess (2) reported that the presence of carbon dioxide in solution increased the solubility and availability of the phosphorus in both di- and tri-calcium phosphates. In the presence of black alkali, however, there was no free carbon dioxide, and the solvent action of carbon dioxide was eliminated.

Plummer (13) applied carbon dioxide-saturated water to soils, some of which had been treated with lime. He observed a marked increase in soluble phosphorus in the unlimed soils but a decreased solubility in the limed soils.

Truog (15) studied the action of decomposing organic matter on the solubility of soil phosphates. He believed that the increase in soluble phosphorus was due to the carbon dioxide produced.

Bauer (1) observed that decaying organic matter produced a solvent action upon rock phosphate. This he believed was due to the action of the organic acids produced in the decomposition of the organic matter.

Parker (11) studied the relation between the production of carbon dioxide and the absorption of phosphorus by plants. He found no appreciable difference between the phosphorus content of the plants on the treated and the untreated soils. In his later studies (12) he indicated that the solvent action of carbon dioxide on phosphorus was not sufficient to explain the absorption of phosphorus from many soils.

McGeorge (7, 9) and Breazeale and McGeorge (3) concluded that carbon dioxide is an important factor in governing the pH and the solubility of phos-

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phorus in the soil. Hoagland and Sharp (4), however, found no appreciable effect of carbon dioxide on the pH of the soil.

The rôle of carbon dioxide in bringing phosphorus into solution has been investigated widely, and the general belief is that carbon dioxide increases the availability of phosphorus in the soil. The literature reviewed, however, shows some difference of opinion on the subject. Most of the work reported dealt with the solubility effects of carbon dioxide-saturated water on phosphate minerals, but some work has been done on the absorption of phosphorus by plants grown in soils containing different amounts of carbon dioxide. The effect of carbon dioxide on the availability of phosphorus was measured by the amount of phosphorus taken up by the plants. Only a comparatively small amount of work has been done on the effect of carbon dioxide as a gas or in solution on the availability of phosphorus in soils; the purpose of this investigation was to obtain some data along this line on certain Iowa soils variously treated.

EXPERIMENTAL

The effects of carbon dioxide on the pH of the soil and on the solubility of phosphorus in soils was studied in two experiments.

In experiment 1, 39 pounds of Carrington loam was placed in each of 16 four-gallon pots and treated in quadruplicate as follows: A—No treatment; B—0.2 per cent oat straw; C—0.2 per cent oat straw + 0.2 per cent rock phosphate; D—0.2 per cent oat straw + 0.2 per cent rock phosphate + 0.1 per cent limestone.

The 16 pots of soil were arranged in four series, each containing one pot of soil from each treatment. In series 1 the soil received no further treatment and served as checks. Carbon dioxide-saturated water, referred to as carbonic acid and having a pH of 4.2, was added to the soils in series 2. In series 3 carbon dioxide gas was added to the soils from below at the rate of 5 liters per hour for 1 hour each day throughout the experiment. The soils in series 4 received a mixture of 1 part oxygen to 4 parts nitrogen gas, also added at the rate of 5 liters per hour for 1 hour each day throughout the experiment. The gases were regulated by means of flow meters (14). The moisture content of the soils was adjusted to 20 per cent and maintained at this amount by frequent additions of distilled water, except in the case of series 2 where carbonic acid was used.

The soils were sampled at intervals for the determination of pH and soluble phosphorus. The pH was determined on the air-dried soils by the quinhydrone electrode, and the soluble phosphorus, by the 0.002 *N* sulfuric acid method.

The soils used in experiment 2 were the Carrington and Tama silt loams. The Carrington silt loam had a pH of 4.93 and a lime requirement of 3 tons per acre. The Tama silt loam had a pH of 5.13 and a lime requirement of 3 tons per acre. The soils were taken from the surface to a depth of about 8

inches, sieved through a one-fourth inch screen, thoroughly mixed, and placed in 4-gallon pots.

Three series of treatments were made, each consisting of 8 pots of each soil. Series 1 was a check and received no treatment. Series 2 received carbon dioxide-saturated water. Series 3 received carbon dioxide gas at the rate of

TABLE 1

Effect of carbon dioxide on soil reaction

SOIL TREATMENT	DATE OF SAMPLING	SERIES			
		Check	Carbonic acid	CO_2 gas	Oxygen + nitrogen
		pH	*pH*	*pH*	*pH*
None	November	6.33	6.33	6.33	6.33
	December	6.09	6.27	6.22	6.00
	January	6.23	6.06	6.31	6.28
	February	6.24	6.24	6.20	6.23
	March	6.30	6.32	6.25	6.29
	April	6.31	6.27	6.37	6.33
Straw	November	6.33	6.33	6.33	6.33
	December	6.35	6.55	6.36	6.24
	January	6.47	6.46	6.52	6.40
	February	6.28	6.17	6.45	6.13
	March	6.12	6.47	6.27	6.41
	April	6.40	6.50	6.50	6.41
Straw + PO_4	November	6.33	6.33	6.33	6.33
	December	6.37	6.60	6.41	6.28
	January	6.47	6.57	6.57	6.31
	February	6.15	6.45	6.32	6.27
	March	6.20	6.43	6.42	6.12
	April	6.45	6.73	6.56	6.33
Straw + PO_4 + Lime	November	6.33	6.33	6.33	6.33
	December	7.09	6.97	6.95	6.83
	January	6.83	6.83	6.80	6.83
	February	6.95	6.81	7.07	7.03
	March	6.99	7.02	6.86	6.96
	April	7.09	7.09	7.01	7.06
Average.....		6.44	6.50	6.48	6.42

5 liters per day to each pot. The carbon dioxide gas was applied continuously to the soil by means of a small glass tube which entered at the base and extended to the center of the pot. The same apparatus was used in applying the gas to the soil as was used in experiment 1, except that test tubes instead of flow meters were used to regulate the rate of flow of the gas. This provided a

convenient method of allowing very small quantities of gas to flow continuously into the soil. The following treatments were made in duplicate to each series: No. 1—No treatment; No. 2—1000 pounds/acre of rock phosphate; No. 3—500 pounds/acre of potassium chloride; No. 4—3 tons/acre of limestone.

The lime added to the soil was 91.3 per cent calcium carbonate and was ground to pass the 200-mesh screen. The materials were added to the soil and thoroughly mixed. The moisture content of the soil was adjusted to 20 per cent and maintained at this amount by frequent additions of water. Distilled water was added to series 1 and 3, and carbon dioxide-saturated water was added to series 2. Samples were taken at monthly intervals for determinations of pH and soluble phosphorus.

TABLE 2

Analysis of variance of pH of Carrington loam variously treated

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE
Between series	3	0.1349	0.0450*
Between treatments	3	5.9753	1.9918*
Between dates	4	0.2143	0.0536*
Interactions:			
Date x series	12	0.1347	0.0112
Date x treatment	12	0.2696	0.0225*
Series x treatment	9	0.1930	0.0214*
Date x treatment x series (experimental error)	36	0.2286	0.0064

* Highly significant.

RESULTS

Experiment 1

Reaction. The hydrogen ion determinations were made by the quinhydrone electrode method using a 10-gm. sample of air-dry soil and 25 cc. of distilled water. The procedure suggested by the Committee of the International Society of Soil Science (5, 6) was followed throughout the experiment. The results are given in tables 1 and 2.

The data in table 1 show that the carbon dioxide gas and the carbonic acid decreased the hydrogen ion concentration of the soil slightly. The analysis of variance[2] (table 2) shows that the difference in pH of the soils in the different series is highly significant. The treatment with nitrogen and oxygen resulted in an increase in the hydrogen ion concentration, but the amount was not significant. There was a significant increase in the mean pH of the soils treated with straw, with straw and phosphate, and with straw, phosphate, and lime, over that of the untreated soil. The mean difference in pH of the soils

[2] Analysis of variance made by the Statistical Laboratory, Iowa State College, Ames, Iowa.

at the different dates was highly significant. The interaction between the different series at the different sampling dates was not significant. That is, there was a distinct trend for all soils treated with carbon dioxide gas or carbonic acid to decrease the hydrogen ion concentration at each sampling. The

TABLE 3

Effect of carbon dioxide on the availability of phosphorus in Carrington loam

SOIL TREATMENT	DATE OF SAMPLING	SERIES			
		Check	Carbonic acid	Carbon dioxide gas	Nitrogen + oxygen
		p.p.m. P	*p.p.m. P*	*p.p.m. P*	*p.p.m. P*
None	November	19.23	19.23	19.23	19.23
	December	18.33	21.51	19.41	19.23
	January	17.85	19.61	19.23	18.54
	February	17.24	18.23	19.37	19.42
	March	17.87	23.43	21.13	19.11
	April	18.24	20.20	23.86	18.88
	Average	17.91	20.56	20.60	19.04
Straw	November	19.23	19.23	19.23	19.23
	December	16.12	19.61	20.88	17.71
	January	13.51	21.33	20.00	17.78
	February	15.87	22.43	20.00	18.18
	March	15.88	20.00	19.67	19.23
	April	16.66	23.46	18.75	17.69
	Average	15.61	21.37	19.86	18.12
Straw + PO_4	November	19.23	19.23	19.23	19.23
	December	24.19	41.68	37.04	28.29
	January	28.06	38.48	38.51	33.48
	February	32.60	38.54	37.59	36.36
	March	36.51	41.08	43.48	36.61
	April	30.96	35.71	37.95	36.15
	Average	30.46	39.10	38.91	34.18
Straw + PO_4 + lime	November	19.23	19.23	19.23	19.23
	December	34.09	41.68	41.78	39.23
	January	28.99	47.61	35.08	29.41
	February	33.33	42.37	39.00	41.06
	March	35.41	46.25	42.00	38.96
	April	34.88	43.61	37.53	40.00
	Average	33.34	44.30	39.08	37.73

interaction between series and treatment, however, was highly significant, indicating a failure of the soils in the different series to react in the same way with different treatments. There was also a failure of a given treatment to produce the same reaction at the different samplings. For instance, there was a significant increase in pH of the check soil at the March sampling, whereas the

soil treated with the straw and phosphate was significantly more acid at the March sampling than at the beginning of the experiment.

Soluble phosphorus. The data in tables 3 and 4 show a highly significant difference in the amount of soluble phosphorus in the soils of the various series. The carbonic acid treatment was most effective in increasing the amount of soluble phosphorus. However, there was a significant interaction between the average phosphorus content of the soils variously treated in the different series. In the untreated soil, the average phosphorus content of the soils in series 2 (nitrogen + oxygen) was not significantly different from that of series 1 (check), but the phosphorus content of the soils in series 3 and 4 was significantly higher than that of the check soil. In the straw-treated soils there was a significant increase in the soluble phosphorus in each series over that of the

TABLE 4

Analysis of variance of p.p.m. soluble phosphorus in Carrington Loam

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE
Between dates	4	165.1051	41.2763†
Between treatment	3	13155.3022	4385.1001†
Between series	3	1105.3022	368.4340†
Interactions:			
Date x treatment	12	255.3736	21.2811*
Date x series	12	99.1636	8.2636
Series x treatment	9	256.5753	28.5084†
Date x series x treatment (experimental error)	36	309.2220	8.5895
Between classes	79	15346.0420	194.2537
Within	80	133.4461	1.6681
Total	159	15479.4881	.....

* Significant.

† Highly significant.

check, the carbonic acid treatment producing the greatest increase. In the soil treated with straw and phosphate there was a significant increase of soluble phosphorus in all series over that of the check, but the carbon dioxide gas was most effective, the difference between the average phosphorus content of the carbonic acid and carbon dioxide-treated soils being small. There was a relatively large increase in soluble phosphorus in the soils treated with straw, phosphate, and lime in all series over that of the check, the carbonic acid treatment again being the most effective. The interaction, date x treatment, was just significant; the straw + phosphate-treated soils contained more soluble phosphorus at the January sampling than at the December sampling, whereas the straw + phosphate + lime-treated soils contained a lower amount of soluble phosphorus at the January sampling than at the December sampling. The interaction, date x series, was not significant, showing that the differences

in soluble phosphorus content of the soils in the different series was approximately the same at the different sampling dates.

Experiment 2

The pH of the Carrington silt loam at the different samplings is shown in table 5, and the pH of the Tama silt loam is given in table 6. The p.p.m. of soluble phosphorus of Carrington silt is presented in table 7, and of Tama silt loam, in table 8. The analysis of variance of the data is given in tables 9 and 10.

Reaction. The data in the tables show that carbon dioxide, either as carbonic acid or as gas, decreased the hydrogen ion concentration of the soil by

TABLE 5

Effect of carbon dioxide on the pH of Carrington silt loam

TREATMENT	SERIES											
	Check				Carbonic acid				Carbon dioxide gas			
	December	January	February	March	December	January	February	March	December	January	February	March
	pH	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*
No treatment	5.43	5.12	5.14	5.17	5.18	5.11	5.18	5.17	5.20	5.13	5.25	5.17
	5.40	5.11	5.13	5.18	5.18	5.14	5.23	5.17	5.22	5.04	5.28	5.17
Rock phosphate	5.30	5.13	5.35	5.23	5.37	5.11	5.30	5.19	5.28	5.11	5.30	5.18
	5.25	5.10	5.30	5.18	5.35	5.08	5.23	5.19	5.34	5.14	5.25	5.21
KCl	5.20	5.14	5.23	5.13	5.11	5.08	5.23	5.10	5.15	5.06	5.17	5.12
	5.13	5.11	5.22	5.13	5.15	5.16	5.15	5.12	5.11	5.06	5.23	5.13
Lime	5.61	5.53	5.71	5.85	5.83	5.84	5.93	5.96	5.74	5.89	6.04	5.96
	5.76	5.58	5.77	5.84	5.81	5.82	5.91	5.92	5.76	5.84	6.03	5.94

an amount not quite significantly different from that of the check soil. There was no significant interaction between soil type and series, indicating the same effect of carbon dioxide on the two soils. However, there was a significant interaction between soil type and soil treatment, indicating a different effect of the soil treatment on the pH of the two soils. For example, the net effect of carbon dioxide or carbonic acid was a decrease in hydrogen ion concentration. However, in the Carrington silt loam this effect was evident only in the limed soil; there was actually a decrease in the pH of the potassium chloride-treated and of the untreated soils which received carbonic acid. In the Tama soil the carbonic acid and carbon dioxide decreased the hydrogen ion concentration of both the rock phosphate and the limed soils, but there was a significant decrease in the pH of the potassium chloride-treated soil.

In general, there was a greater difference in the pH of the soils one month after treatment than at the other samplings, and the significant interactions

TABLE 6

Effect of carbon dioxide on the pH of Tama silt loam

TREATMENT	SERIES											
	Check				Carbonic acid				Carbon dioxide gas			
	December	January	February	March	December	January	February	March	December	January	February	March
	pH	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*	*pH*
No treatment	5.00	5.06	5.06	5.09	5.15	5.01	5.00	5.09	5.17	4.97	4.98	5.14
	5.16	5.02	5.03	5.08	5.23	5.06	5.00	5.13	5.10	5.02	5.00	5.18
Rock phosphate	5.17	5.06	5.08	5.18	5.14	5.23	5.08	5.15	5.19	5.28	5.17	5.14
	5.15	5.01	5.12	5.17	5.18	5.21	5.12	5.18	5.13	5.21	5.13	5.18
KCl	5.10	5.14	5.15	5.20	5.08	5.06	5.12	5.15	5.15	5.08	5.17	5.19
	5.12	5.19	5.15	5.19	5.10	5.02	5.17	5.19	5.15	5.04	5.34	5.15
Lime	6.23	5.60	5.81	5.83	6.08	5.63	5.81	5.95	6.27	5.82	5.93	6.05
	6.15	5.67	5.76	5.86	6.10	5.68	5.84	6.00	6.38	5.80	5.91	6.11

TABLE 7

Effect of carbon dioxide on the solubility of phosphorus in Carrington silt loam

TREATMENT	SERIES											
	Check				Carbonic acid				Carbon dioxide gas			
	December	January	February	March	December	January	February	March	December	January	February	March
	p.p.m. P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P
No treatment	10.1	8.7	10.0	9.1	11.9	8.7	10.1	10.0	11.7	8.7	9.7	9.9
	10.4	9.0	10.7	9.3	12.4	8.7	10.1	9.7	12.1	9.0	9.7	9.8
Rock phosphate	37.3	39.1	36.5	38.0	38.1	40.1	40.0	41.0	39.8	46.0	41.3	42.0
	38.3	38.3	37.3	37.0	39.3	43.7	41.8	41.5	39.6	45.3	41.8	42.5
KCl	13.6	10.3	9.7	10.0	13.0	10.6	9.4	11.3	13.3	11.1	10.0	12.9
	13.6	10.9	9.4	10.4	13.7	10.6	9.7	11.1	13.1	10.9	10.1	12.6
Lime	12.9	11.2	10.0	9.7	12.7	11.2	12.4	11.0	13.1	11.5	12.1	11.1
	13.1	11.5	10.4	10.0	13.0	11.4	12.0	10.9	13.0	11.3	12.1	11.4

between date and soil treatment and date and series indicate that the two soils did not react in the same way nor was the effect of treatment the same at the various dates.

The difference in the effect of carbon dioxide on the pH of the two soils may be explained on the basis of the buffering capacity of the two soils. Breazeale and McGeorge (3) and McGeorge (8) have reported an increase in the hydrogen ion concentration of alkali soils by treatment with carbon dioxide. Hoagland and Sharp (4), from work on different soils, concluded that carbon dioxide was without appreciable effect on the reaction. The data presented here indicate an increase in the pH of the Carrington loam and of the Tama and Carrington silt loams, especially when the soils have been treated with calcium phosphate or calcium carbonate. This may be explained if it is assumed that the carbon dioxide and the carbonic acid bring about a hydrolysis of the amino acids of the organic matter, thus liberating ammonia which ionizes to give the OH^- ion.

TABLE 8

Effect of carbon dioxide on the solubility of phosphorus in Tama silt loam

TREATMENT	SERIES											
	Check				Carbonic acid				Carbon dioxide gas			
	December	January	February	March	December	January	February	March	December	January	February	March
	p.p.m. P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P	*p.p.m.* P
No treatment	50.0	33.0	39.7	38.8	50.0	35.1	40.8	39.7	54.1	36.5	43.1	41.0
	46.5	33.5	40.0	39.1	54.1	35.0	40.8	39.8	56.6	36.6	42.7	40.8
Rock phosphate	95.5	69.5	69.4	70.9	112.3	73.8	71.4	82.0	86.5	65.6	73.0	76.9
	102.0	63.1	68.5	70.4	105.2	74.8	73.0	80.7	88.5	68.3	74.1	76.3
KCl	49.5	37.2	43.5	49.0	52.6	39.5	43.9	49.8	48.1	40.2	45.3	50.3
	50.0	37.4	43.9	49.5	51.0	39.5	44.4	49.5	48.5	41.1	45.5	49.5
Lime	47.8	40.1	51.6	43.5	51.8	41.0	46.3	43.5	52.4	42.8	46.5	44.4
	47.3	40.4	51.0	43.1	54.3	41.5	46.3	43.1	53.4	43.6	47.0	44.8

The Carrington silt loam, which is less well buffered than the Tama silt loam and also less well supplied with organic matter, does not increase in pH upon treatment with carbon dioxide or carbonic acid. The exchange acidity developed by treatment with potassium chloride was sufficient to decrease the pH of both soils regardless of the effect of carbon dioxide.

Soluble phosphorus. The data in tables 7, 8, 9, and 10 show that carbonic acid and carbon dioxide were effective in both the Carrington and Tama silt loams in increasing significantly the amount of phosphorus soluble in 0.002 *N* sulfuric acid. The difference in the effectiveness of the carbon dioxide and the carbonic acid in dissolving the phosphorus was not significant. Treatment of the soil with rock phosphare, potassium chloride, or lime was slightly more effective in the Tama silt loam than in the Carrington silt loam. The potassium chloride increased the solubility of the phosphorus significantly.

TABLE 9

Analysis of variance of pH of Carrington and Tama silt loams

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE
Between soil type	1	0.0253	0.0253
Between series:			
($H_2CO_3 - CO_2$)	1	0.0251	0.0251
Check − ($H_2CO_3 + CO_2$)	1	0.0453	0.0453†
Between treatment:			
3L − (NT + RP + KCl)	1	18.8645	18.8645†
2RP − (NT + KCl)	1	0.0942	0.0942*
NT − KCl	1	0.0036	0.0036
Between dates	3	0.4446	0.1482†
Interactions:			
Soil type x series	2	0.0155	0.0078
Soil type x treatment	3	0.3228	0.1076†
Soil type x date	3	0.1400	0.0467
Series x treatment	6	0.2118	0.0353
Series x date	6	0.0229	0.0038
Treatment x date	9	0.2416	0.0268
Error	57	0.8178	0.0143
Total	95	21.2752	.....

* Significant.

† Highly significant.

TABLE 10

Analysis of variance of p.p.m. of phosphorus of Carrington and Tama silt loams

SOURCE OF VARIATION	DEGREES OF FREEDOM	SUM OF SQUARES	MEAN SQUARE
Between soil type	1	58443.5419	58443.5419†
Between series:			
($H_2CO_3 - CO_2$)	1	4.9220	4.9220
Check − ($H_2CO_3 + CO_2$)	1	136.6844	136.6844*
Between treatment:			
3RP − (NT + KCl + L)	1	36236.2950	36236.2950†
2L − (NT + KCl)	1	84.7168	84.7168
NT − KCl	1	158.1068	158.1068*
Between dates	3	1994.9560	664.9853†
Interactions:			
Soil type x series	2	35.3740	17.6870
Soil type x treatment	3	268.5635	89.5212
Soil type x date	3	1531.6602	510.5534†
Series x treatment	6	153.3748	25.5625
Series x date	6	64.3711	10.7285
Treatment x date	9	546.8785	60.7643
Error	57	1539.2748	27.0048
Total	95	101198.7198	.....

* Significant.

† Highly significant.

DISCUSSION AND SUMMARY

Data have been presented which show that soil phosphates are rendered soluble in 0.002 *N* sulfuric acid by carbon dioxide or carbonic acid. It has been generally assumed that this increased solubility of phosphorus results from an increased hydrogen ion concentration of the soil solution brought about by the ionization of carbonic acid. However, data have also been presented which show that carbon dioxide or carbonic acid may result in a decreased hydrogen ion concentration of the soil solution, depending upon the soil type. In the untreated Carrintgon silt loam, carbon dioxide increased the hydrogen ion concentration, but treatment with rock phosphate buffered the solution sufficiently so that there was no effect. The Tama silt loam was sufficiently well buffered without the rock phosphate addition to prevent the carbon dioxide's producing an acid reaction. Rock phosphate and calcium carbonate in the Tama soil with carbon dioxide resulted in a decrease in hydrogen ion concentration as compared with that of the soil treated with these materials but without the carbon dioxide. Since nitrate production was also stimulated in these soils by carbon dioxide (14), it would seem that the increase in pH was due to a hydrolysis of the ammonifiable and nitrifiable organic matter. The increased solubility of phosphorus in these cases is certainly not due to an increased hydrogen ion concentration but may be explained on the basis of the production of more soluble forms of phosphorus coincident with the change in soil reaction. Thus, the net effect of carbonic acid or carbon dioxide is an increased solubility of the phosphorus, regardless of the effect of the carbon dioxide on soil reaction. This is further emphasized by the fact that the correlation between the pH of the soil and the phosphorus soluble in 0.002 *N* sulfuric acid was not significant.

Carbon dioxide was more effective in increasing the solubility of phosphorus in the untreated Carrington silt loam than was the carbonic acid, but the reverse relation was found in the untreated Tama silt loam. In the rock phosphate-treated soils the carbonic acid was more effective than carbon dioxide in the Carrington silt loam, but again the reverse relation obtained in the Tama silt loam. In other words, treating the Carrington silt loam with rock phosphate caused it to react to carbonic acid in the same way as the untreated Tama silt loam. This treatment also caused the same directional change in pH of the two soils. This does not seem to be an important point but it serves to emphasize the fact that carbon dioxide may have different effects in different soils and also that the forms of phosphorus in the two soils may be very different.

The results obtained with 0.002 *N* sulfuric acid as the extractant of the phosphorus are perhaps different from those that would have been obtained with any other extractant. However, the fact that carbonic acid or carbon dioxide increased the solubility of the soil phosphorus in this relatively strongly acid solution would seem more significant than if similar results had been obtained with a less acid solution as the extractant.

REFERENCES

(1) BAUER, F. C. 1921 The relation of organic matter and the feeding power of plants to the utilization of rock phosphate. *Soil Sci.* 12: 21–41.

(2) BREAZEALE, J. F., AND BURGESS, P. S. 1926 The availability of phosphates in calcareous or alkaline soils. Ariz. Agr. Exp. Sta. Tech. Bul. 10.

(3) BREAZEALE, J. F., AND MCGEORGE, W. T. 1932 Nutritional disorders in alkaline soils as caused by a deficiency of carbon dioxide. Ariz. Agr. Exp. Sta. Tech. Bul. 41.

(4) HOAGLAND, D. R., AND SHARP, L. T. 1918 Relation of carbon dioxide to soil reaction as measured by the hydrogen electrode. *Jour. Agr. Res.* 12: 139–148.

(5) International Society of Soil Science 1930 Second Commission. Report of the Committee on Soil Reaction Measurements: I. Results of comparative investigation on the quinhydrone method. *Soil Res.* 2: 77–139.

(6) International Society of Soil Science 1930 Second Commission. Report of Committee on Soil Reaction Measurements: II. Conclusions and recommendations. *Soil Res.* 2: 141–152.

(7) MCGEORGE, W. T. 1933 Phosphate availability in alkaline calcareous soils. *Jour. Amer. Soc. Agron.* 25: 351–354.

(8) MCGEORGE, W. T. 1935 The relation of potential alkalinity to the availability of phosphorus in calcareous soils. *Soil Sci.* 38: 443–452.

(9) MCGEORGE, W. T. 1935 Phosphate availability in alkaline calcareous soils: A function of carbon dioxide and pH. *Jour. Amer. Soc. Agron.* 27: 330–335.

(10) MCGEORGE, W. T., AND BREAZEALE, J. F. 1932 Studies on iron, aluminum and organic phosphates and phosphate fixation in calcareous soils. Ariz. Agr. Exp. Sta. Tech. Bul. 40.

(11) PARKER, F. W. 1924 Carbon dioxide production of plant roots as a factor in the feeding power of plants. *Soil Sci.* 17: 229–248.

(12) PARKER, F. W. 1927 Soil phosphorus studies: III. Plant growth and the absorption of phosphorus from culture solutions of different phosphate concentrations. *Soil Sci.* 24: 129–145.

(13) PLUMMER, J. K. 1918 Availability of potash in some common soil-forming minerals. Effect of lime upon potash absorption by different crops. *Jour. Agr. Res.* 14: 297–316.

(14) SMITH, F. B., BROWN, P. E., AND MILLAR, H. C. 1937 Some effects of carbon dioxide on the decomposition of organic matter and the accumulation of nitrates in the soil. *Soil Sci.* 43: 15–25.

(15) TRUOG, E. 1912 Factors influencing the availability of rock phosphate. Wis. Agr. Exp. Sta. Bul. 20.

GENERAL TRENDS OF THE DESERT TYPE OF SOIL FORMATION

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The region where this investigation was conducted is a part of the great American Desert known as the Great Basin region. This desert, in turn, is a part of the great geographical belt, or zone of the deserts, which extends through the southwestern part of North America, northern Africa, Arabia, Asia Minor, and central Asia.

These studies were centered mainly in the deserts of southeastern California, western Arizona, and the southern parts of Nevada and Utah. This area comprises a region known as the Mojave Desert, and a part of it extends into the Colorado Desert. The territory has been characterized by Marbut (5) as a region which "consists topographically of a series of isolated, short, north-south mountain ranges separated by long alluvial fans stretching from the mountains outward, the fans from adjacent parallel ranges meeting along the axial line of the lowland belt separating the mountains. In places where the fans do not actually meet along the axial line of the lowland, they are separated along this line by a flat area which is usually subjected to flooding and known as a playa. The playas constitute, however, a very unimportant part of the whole region."

One may assume that this region is in a constructive process of a progressive peneplanation. Because of the climatic conditions of the desert, characterized by a restricted rainfall, spontaneous cloudbursts, and the great and rather sharp diurnal changes of temperature; of the sharp and, in many places, abrupt contours of the mountain ridges; and of their general petrographic composition, mechanical disintegration of the bedrocks proceeds far in advance of the chemical decomposition of the debris produced by physical weathering. The steep broken slopes of the mountains and the frequently torrential nature of the summer rains promote very rapid removal of the deconsolidated debris from the slopes and the construction of the huge "alluvial fans" at the foot of the mountains, thereby continually denuding and exposing the fresh surfaces of the bedrocks to further attacks by the physical forces of the climate (pl. 1, figs. 1 and 2). The debris removed from the mountain slopes does not travel far from the place of origin. The torrential and intermittent streams lose their driving force as soon as they emerge from the mouths of the canyons and spread their mineral burden over the broad gently sloping surface of the fans. Only a few continuously flowing rivers traverse the expanses of desert, erode the valleys, and move the unconsolidated deposits farther away. As only a very

small part of the total bulk of debris annually washed off the mountains and deposited in the intermountain depressions undergoes farther transportation and redeposition, the continually growing alluvial fans gradually fill up the depressions and basins.

The geomorphological construction of the land surface, as outlined above, is not a typical feature of the entire desert belt. As Marbut states (5), this landscape characterizes "that part of the Great Basin region extending approximately from the northern boundary of Nevada southward or southeastward as far as the Desert soils are known to occur."

The mountain ranges, most of which are composed of granite and closely related rocks or of basalts, vary in elevation from a few hundred to several thousand feet above the average level of the broad intermountain depressions. They are characterized by steep, very rocky, and strongly eroded slopes, and their bases are buried under the thick deposits of the adjacent fans. Generally the mountains rise abruptly from the surrounding gently sloping plains. The main axes of the ranges vary from one or two to many miles in length, whereas the axes perpendicular to the main ones extend from just a fraction to several miles. According to Marbut (5) "the mountains as a rule contain no soil, or an extremely thin layer of soil" and "are either entirely bare or are covered with a very thin cover of brush except a few ranges much higher than the average, on which open forests are growing." Many of them, especially those composed of granitic rocks, appear as huge piles of rocks roughly rounded by wind corrosion and heavy rains. Only occasionally here and there among the bare rocks one steps on a flat, step-like spot, just a few square yards in area, which is covered by coarse angular grit well compacted by rains. Such spots appear more frequently and are of larger dimensions near the tops of the mountains, especially on the somewhat rounded passes. These local accumulations of grit are nowhere thick; just a foot or two below the surface the deconsolidated grit grades into decayed bedrock. Actually no real soil formation takes place here, however, but one usually observes that a little below the surface the color of the gritty material becomes somewhat redder than that on the surface, and the general composition of the mass becomes more clayey and somewhat more compact. Usually all this appears just above the surface of decayed bedrock, which also is penetrated by a number of bright brownish red or purplish red veins and films developed along the occasional fissures. This development, which will be discussed later in this paper, apparently is a result of a hydrolitic decomposition of certain minerals, such as feldspars and hornblende, and a subsequent dehydration of certain iron-bearing products of this action.

The intermountain basins vary from less than one to more than twenty miles across their main axes, and a number of them extend many miles in length. In the Pleistocene period and immediately afterward some of them were occupied by a number of inland seas and lakes, of which Bonneville and Lahonton Lakes were the most prominent. At the present time most of the basins are occupied by alluvial fans which are the most striking and typical feature of the

entire region. These fans stretch outward from the mountains or hills in all directions so that they encircle the bases of isolated groups of mountains by the broad, gently sloping, and generally smooth-surfaced plains (pl. 1, figs. 3 and 4). They extend for a distance ranging from less than one to more than ten miles from the mouths of the canyons from which their material has been flushed into the basins. This material consists of an unassorted drift composed of boulders, coarse gravel, or angular fragments of rocks, grit, sand, and silt. In some places it is known to form deposits several hundred feet thick. Marbut (5) states that "the alluvial fans are in process of development, but deposition of material from which they develop does not take place over the whole surface of the fan at any one time. The streams which carry material from the mountains during the occasional desert thunderstorms onto the alluvial fans shift from time to time and eventually distribute the material over whole fan. In some part of every fan, therefore, the material is now accumulated or has accumulated so recently that no soil profile development has taken place. In other parts of the fans accumulation took place a long time ago."

The outstanding feature of by far the greater majority of the individual soil types in the desert alluvial fans is that the upper section of their profiles is hardly even touched by a strictly soil-forming process. Generally it is just a mechanical layer of an unassorted and more or less recently deposited drift. Its surface is marked almost everywhere by the strong, sometimes violent, runoff caused by the last cloudburst, or by the wind drift caused by the last sand and dust storm. The thickness of this rough overwash or drift varies from less than one foot to many feet, according to the course of the mud stream which spreads its burden over the fan. The only modification of this layer is an occasional development of the desert pavement which will be described later. Another striking characteristic of the soils of alluvial fans, as well as of many other desert regions, is a frequent and strong development of hardpans at some depth from the surface.

The playas, or flat and dry basins of the former lakes, as well as the flood plains and lower terraces of the desert valleys, represent a third individual geomorphological landscape. Much of this land is occupied by large tracts of the typical Solonchacks (pl. 3, figs. 1, 2, and 3), which belong to a group of intrazonal soils, and also by the azonal valley soils, which often are spoken of as "alluvial" soils.

The three individual landscapes briefly outlined do not cover the entire geomorphological complex of the desert. A number of others are easily recognizable. A large group of soils, developed predominantly from residual materials, occupies the expansive lava beds, broad basaltic table mountains and plateaus, gently rolling to hilly plateaus of the granitic rocks or of basalts, sandstones, limestones, or clays. By far the greater part of these lands is covered by a very thin mantle composed of the unconsolidated products of weathering. In many places this does not exceed one foot in thickness, with frequent exposure of the entirely bare rocks. A thickness ranging from two

to four feet may be considered as close to the average. This mantle is underlain by the decayed and semi-deconsolidated rocks, as granites, diorites, sandstones, and others, or by the coarsely fragmented rocks, such as basalts, lavas, etc. Profile development in most of these soils is, as a rule, very weak, although occasionally a certain concentration of lime can be found at some depth from the surface. Usually this lime forms a coating or even crusts on the fragments of rocks, and conspicuously such crusts do not completely envelop the stones but occur only on the lower portion in their natural position. In a few places the lime was found in a quantity sufficient to cause cementation of the entire layer from a few inches to more than one foot into a conglomerate-like crust. No lime, however, was observed in the regions of the granite and related rocks, but locally it appears in the soils derived from the basalts and lavas, although apparently only in places when these rocks are closely associated or are underlain by limestones or some other lime-containing formations.

Despite the considerable variety of the underlying bedrocks, topography, past history, and other local features in different parts of the desert, its general character remains fairly uniform throughout the entire extent of this geographic belt. One of the principal characteristics of the desert is that it is a natural region of exceedingly low biological pressure, which in turn is a natural consequence of climatic conditions decidedly unfavorable for biochemical activity: a deficiency of moisture is the principal limiting factor. These two—scarcity of moisture and low biological pressure—appear to be the determining factors in the process of the development of the Desert soils.

An outstanding feature of the Desert type of soil formation, in which it differs from the other zonal types rather sharply, is that the direct influence of the climate on soil formation seems to be much stronger than that of living nature: it is predominantly an abiotic type. Among the climatic factors, the principal ones are precipitation and temperature. In the temperate belt and in all humid climatic provinces the amount of precipitation, as well as its character and annual distribution, appears as the leading climatic factor of soil formation, with the temperature playing a rôle of rather secondary importance. In the Desert soil zone, however, the amount of rainfall is reduced to a very low limit, which greatly diminishes the constructive activity of this factor. Consequently temperature begins to dominate the other climatic forces in a Desert soil-forming process which can be more definitely designated as predominantly abiotic and termogenic. In this respect one may find a certain similarity in the general character of the soil-forming processes in the hot Desert and the cold Desert or Tundra.

The mean annual rainfall in the desert regions is naturally low. For most of the desert it is less than ten inches. Two quite distinct rainy seasons characterize the climate of the desert area under discussion—winter and summer. The first of these is characterized by the gentle and rather prolonged rains, whereas the summer rains are of a spontaneous and stormy nature and of short duration. These two rainy seasons are separated by dry intervals, and of

these two, the especially rainless season is the spring and early summer period, which continues through April, May, June, and most commonly July. A high temperature prevails throughout this season and is accompanied by rather strong winds which may continue for several days or even weeks and reach a high velocity, causing strong destructive sand drifts.

The fact that a period of the gentle and prolonged rains of a relatively warm winter is followed by a hot, long, rainless, and windy season, which in turn is followed by a season of irregular and not infrequently torrential rains, is of primary importance for the evolution of the physiographic landscape of the desert.

During the winter period, when from 30 to 50 per cent of the annual rainfall occurs, there is little if any run-off from the surface. The soil retains most of this water and becomes moist to a depth of several feet. This is sufficient to support a spectacular and occasionally even luxuriant outburst of the short-lived spring vegetation. The desert actually may be covered by a variety of flowering plants (pl. 2, fig. 1). This period, however, does not last long—hardly more than a few weeks. The dry heat of the next rainless and windy season rapidly kills the tender spring plants and flowers. Only sparsely growing and deeply rooted desert shrubs, such as creosote bush and sage, and a few of the most resistant bunch grasses, survive. The surfaces of the wide interbrush areas become practically bare (pl. 2, fig. 1). The soil, especially its relatively loose upper section, dries quickly. Its loose composition and rather coarse gritty texture provide very good aeration which facilitates and stimulates very rapid and apparently complete decomposition and mineralization of the scant organic residue left by the spring flora. The dry leaflets and stems left on the surface are fragile and crumbly; they are easily broken, detached from the soil and drifted by wind from the smooth and bare surface. Even those which may be left will be washed away by the next cloudburst. Consequently, soon after the beginning of the dry season, and a long time before it ends, the organic residues of the spring flora disappear from the soil. This is one of the fundamental characteristics of the Desert type of soil formation.

The typical Desert soils not only do not accumulate humus but, strictly speaking, do not contain any humus. In this respect they differ strikingly from the soils of the neighboring zone of the grassland type. A brief comparison of the two—the Desert and the Steppe—will bring about a clearer individuality of the former and of its principal zonal feature. The duration of the vegetative period in the grassland is determined by the spring and fall frosts. There is an annual winter interval dominated by low temperature, during which the biochemical activity in the soil is comparatively dormant and the soil is covered with snow. The vegetative period, at least a large part of it, is supplied with enough rainfall to allow a prolonged growth of grass vegetation. The grasses form a continuous sod and build up a considerable amount of green matter. The later part of the frost-free period may be dry, during which time a vegetative development and growth can discontinue before the

winter season begins. The interval, however, between the end of the growing period (due to a lack of moisture) and the beginning of the winter frost and snowfall is far from being sufficiently long and favorable for rapid decomposition of the dry residues. The dry and rather soft grass attached by roots to the sod forms a soft mat which soon will be covered and somewhat compressed by the snow and thoroughly wetted by its thawing in the spring. By far the greater part of the residues of the yearly crop of living matter remains in and on the soil undecomposed or only slightly decomposed, until the beginning of the next vegetative period. The active decomposition of these residues develops simultaneously with the outbreak and development of the next crop. Consequently the biopedogenic cycles which begin each spring do not come to a close within one year, but most of the phases of decomposition extend into the following years, and this results in the accumulation of humus until a certain equilibrium is reached.

As compared with this, the Desert undergoes hardly any interruption of the vegetation period on account of frosts. Its vegetative period, however, is much shorter than that of the Steppe, and its duration is determined by the occurrence of rainfall. Only a relatively small number of specifically adapted species of plants survive in the Desert; they do not form a sod, and they produce a comparatively small amount of green matter. The period of the production of green material is not followed by the cold season which would retard the decomposition; on the contrary, it is followed by a hot period stimulating rapid decomposition. Consequently each annual biopedogenic cycle ends within one year and usually long before the outbreak of the next cycle, which prevents the formation of humus. This is, however, a somewhat idealized case; the desert vegetation is not composed of the short-lived spring annuals alone, but includes a group of perennial plants. The latter are represented mainly by the desert shrubbery. The most typical of these are the creosote bush (*Covillea mexicana*), which is a decidedly dominant plant in the southern part of the desert (pl. 2, fig. 3), and the sagebrush (*Artemisia tridentata*), which predominates in the northern part (pl. 2, fig. 4). Creosote bush is the most plentiful and typical plant growing throughout the entire Mojave Desert and most of the Colorado Desert. Not infrequently almost pure stands of this shrub cover large tracts of the desert; more often, however, it forms an association with the sagebrush (*Artemisia Californica Less*) and some other shrubs. It is a diffusely branched, open deciduous, evergreen shrub, from three to ten feet high, although more commonly its height does not exceed five or six feet. An individual shrub may spread its slender airy branches over an area ranging from four to six feet in diameter. As a rule, this plant grows very sparsely, leaving wide, open intervals which may extend for a distance from ten to more than forty feet between one bush and another. This spacing allows free action of the wind and consequently strong wind erosion of the surface soil of the open intershrub areas. In many places the surface of the open tracts is covered by a thin layer of the outblown coarse grit or gravel, and the finer material—sand

and silt—is heaped in small mounds under the bushes. Neither creosote bush nor the other shrubs contribute much to the formation of humus. The small and rather coarse and brittle dry leaflets and dry branches which they drop are drifted by wind or washed away with the other residues left on the surface, and their dying roots decompose as completely as the other subterranean residue and apparently rather rapidly.

In addition to the shrubs, a variety of cacti (pl. 3, fig. 4) and a few other desert plants, such as Yuccas, especially the giant Joshua tree, may be mentioned as the typical plants of the desert.

The sparse growth of the shrubs is responsible for the development of a conspicuous microcomplex of the surface of the desert, which in many places is spotted by the small rounded mounds associated with the individual bushes. These range from slightly more than one foot to only occasionally more than three or four feet in height and from six to about fifteen feet in diameter. It seems almost certain that they were heaped around the shrubs by the wind, originally in the shape of miniature dunes, then reshaped and rounded by rains and run-off. These mounds are composed of much better assorted sandy and silty material. The surface of the mounds in general is soft, and their mass is, as a rule, mellow and even loose to considerable depth, whereas the surface of most of the open intermound "microflats," or depressions, is covered by a somewhat crusty and gravelly desert pavement. This apparently allows the mounds to absorb and conserve more moisture from the transient desert rains, which may be helped to some extent by the shadow from the bush. The drifting winds, which remove the loose residues and seeds from the open tracts, drop some of this material between the stems of the bushes, and the elevation of the mounds protects them from being robbed by the run-off. All this leads to a definite concentration of the vegetation around the shrubs, which in turn attracts and stimulates a concentration of the desert fauna on the same spots. Most of the mounds are marked by a greater activity of the desert rodents, gnawing and burrowing animals—mice, ground squirrels, gophers, etc.—, and also of insects, most of which are living in the soil and depend for sustenance on seeds and roots. These, in turn, keep the soil in a loose condition and fertilize it by their byproducts and finally by their bodies. In this way a certain mutually beneficial symbiosis between the desert flora and fauna becomes established, which utilizes the advantage of the conservation of moisture in the mechanically heaped mounds and aids both in their struggle with the unfavorable desert environment.

The dry rainless and hot period, which follows the winter rainy season, apparently is the season of the most energetic disintegration of rocks and of the most intensive activity of the winds. The summer rains which follow next provide very little benefit, if any, to the desert vegetation. The water from these rains runs off quickly, and the soil does not absorb much of it. A fast run-off without much absorption of water by the soil is accelerated, at least to a certain extent, by the development of the smooth and somewhat compacted

thin surface crust which prevents penetration of water into the lower layers of the soil. The heavy summer showers are very active as an agent of peneplantation of the country; annually they remove a great bulk of debris from the mountain slopes, erode the slopes, and spread the material over the fans, gradually filling up the intermountain basins, but so far as soil formation is concerned they are of a rather destructive nature and act almost exclusively on the remodeling and make-up of the soil surface. A negligible penetration of their water into the soil, followed by almost immediate evaporation of the moisture back into the atmosphere, prevents the possibility of development of any leaching of the surface soil; however, this may be one of the principal factors in formation of the somewhat compacted and assorted surface crust. The winter rains, from which the deeper horizons of the soil collect almost all of their moisture, are, on the contrary, too mild and gentle to furnish enough water for its gravitational penetration through the soil, which in turn makes hardly probable any infiltration of any substances from the surface soil downward, and if any chemical leaching of the soil takes place during this period it must be reduced to an extreme minimum and can affect only the most readily soluble compounds.

This brief discussion of the desert vegetation shows, as stated by Joffe (3, p. 161), that "in the desert and semidesert regions the biosphere as a factor of soil formation is reduced to a minimum." As previously stated, the desert type of soil formation is predominantly of an abiotic type, controlled directly by the forces of climate. A consideration of the character of the precipitation, on the other hand, leads to the conclusion that the rainfall in the desert regions is a powerful factor in the geological evolution of the general landscape but has a comparatively limited constructive influence on the normal soil profile. It is a strong agent in the formation of parent materials and in determining their surface configuration but contributes little to the development of the soil profile itself.

The general character of the Desert type of soil formation apparently is dominated by a certain process which leads to a rather frequent occurrence and a comparatively wide geographical distribution of the formation known as the desert crusts. The proper place of these soils in a general soil classification is not yet sufficiently clear. Glinka put them tentatively into the group of Solonchaks, assuming a probable genetic relationship between the typical Solonchaks and the crusts. According to Glinka (1) "one may recognize at least four types of such crusts, namely a limy crust, a gypsum crust, a silicic crust, and a protective crust." The last of these known also as "desert tan" or "desert varnish," represents a formation decidedly different from the other three. A desert tan does not form a really solid crust similar to those which characterize the desert crusts proper. It appears as a film, hardly ever more than 1 mm. in thickness, of rather dark brown, coffee-brown, or even black color. Less frequently it has a yellow, deep orange-yellow, or reddish color. It forms a somewhat shining (varnished) coating on the rocks, cobblestones,

and gravel exposed to the influence of the sunshine and the desert heat. It has been described by Merrill (7) as "a thin dark varnish-like coating, not inaptly named by Mr. Gilbert 'desert varnish,' and which consists largely of oxides of iron and manganese, though a slight amount of organic matter is present." The desert tan is a common feature in our deserts, and is especially spectacular on the surface of the so-called "desert pavement." This, as described by Marbut (5), "consists of a layer of gravel and small stones, lying practically bare and kept bare of fine material by the wind, which usually forms a rather firm crust capable of bearing some weight, but in most places it is not sufficiently strong to bear the weight of a man. In walking over it, the crust breaks and the gravel forming it sinks half an inch or more, making a well defined track in the pavement. The gravel of the pavement are embedded in a gray, almost white, fine-grained material which is usually extremely porous or vesicular." The term "pavement" apparently was applied for the designation of a smooth, practically continuous thin layer of the gravel accumulated on the surface of the soil, after all the finer material had been blown away by wind, and partly embedded in a thin fragile surface crust which holds it together. In few places is this layer more than a fraction of an inch thick. It is underlain by "extremely porous or vesicular" fine-grained material. This "surface crust" is also a formation different from the desert crusts proper.

The typical desert crusts are known to exist in various widely separated places. Outside of the North American continent they were found in northern Africa (Tunis, Algeria, and Morocco); in Asia they are known in Palestine, Syria, Arabia, and Turkestan; they were also found in the deserts of central Australia and elsewhere.

The outstanding feature of the desert crusts as a type of soil formation is the crust itself, a strongly indurated or cemented horizon commonly known in this country as "hardpan." This hardpan, or crust, varies in thickness from less than one foot to several feet in one solid layer, but in some places it is made up of several relatively thinner layers separated from each other by strata of non-cemented mellow or even loose material. In only a few places is the crust exposed on the surface. In most places it is covered by a mantle of loose or mellow material ranging in thickness from a few inches to several feet, and it is not unusual that there is a rather wide range in thickness within a short distance. Not uncommonly the change from the loose surface cover to the solid crust is rather sharp, whereas the lower boundary of the zone of cementation is much less distinct. In many other cases, however, it was observed that a somewhat compacted, clayey horizon, red or reddish in color, develops above the crust, and, here and there, both these merge into each other without any distinct line of demarkation.

The main characteristic of the crust is its hardness. The typical hardpan is cemented or petrified into a solid mass which retains its firmness under various conditions of moisture and requires blasting in order to break it. This is, however, not an unconditional characteristic. One may assume that such

firm crusts represent an ultimate stage of their development. In many and probably in a majority of cases the crusts are less firm, more crumbly or fragile, or are even only compact rather than hard. In such cases one may assume that a crust, as such, has not been developed, and only the clayey horizon, which is sometimes found above the crust, is present. The soils with a firm hardpan or the true desert crusts occur in a number of isolated tracts scattered over the desert, some of them small and others extending for many miles. Consequently, an occurrence of the solid crust is not a necessary characteristic of all Desert soils. A more general statement, however, seems to be correct: By far the greater majority of the Desert soils are characterized by a development of a certain horizon or zone of compactness, which in many particular cases grades into a cemented layer that not infrequently develops into the firm hardpan, or crust. The exception is found in a group of rather underdeveloped soils derived from recently formed parent materials, such as fresh alluvium of the river bottom land and dry lake basins, or playas, and of some comparatively young terraces. A large part of this land is occupied by soils of the true Solonchak type.

A compactness which, generally speaking, depends on a certain proportion of the fine-textured material, especially clay, that fills the spaces among the coarser soil particles, does not denote the same property which is considered when one speaks about the cementation. A cementation may be performed by clay, but more commonly it is made by materials other than clay, such as lime, gypsum, silica, and perhaps other salts. A certain accumulation of these compounds may produce a strong cementation of the soil mass without a great increase of its compactness, and an increase in the content of clay may increase the grade of compactness without producing any cementation. Therefore, the development of a particular horizon of compactness, which generally is characterized by a texture heavier than that of the other horizons, is not necessarily a result of the same process leading to development of cementation. One may assume an existence of different causes and processes of the development of compactness and cementation in the Desert soils, although very often they accompany each other and, so to say, overlap each other in the soil profile. A zone of compactness, which may be considered a claypan, varies in thickness from less than one to several feet but rather seldom to more than three feet. It may be abruptly separated from the looser material of the horizon above, or this change may be more or less gradual. On drying it becomes hard and not infrequently breaks into vertically oriented coarse angular clods or prisms. This is especially conspicuous when its surface is definite and close to the surface of the soil. Its color usually is darker and brighter than that of the other horizons and more often has a distinct reddish tint, which is especially typical for the soils of the southern deserts.

A cementation of the loose, unconsolidated debris into the solid crust depends, as has been mentioned already, on an increase of clay content and especially on an accumulation of certain chemical compounds. Among these,

lime carbonate, gypsum, and soluble silica are by far the most important. It is almost certain that there exist the pure mono-anion silicic, lime, and gypsum crusts listed in Glinka's classification. In addition to this, however, not infrequently there are found the composite crusts formed by more than one kind of cementing material. The most common crusts in our deserts are the lime-and-gypsum crust (sulfo-carbonate type) and the lime-silicic crusts (strongly, moderately, or slightly calcareous silicic crusts). All these should be recognized as the poly-anion types of Desert crusts.

The concentration of the cementing compounds varies widely in different crusts. Lime carbonate not infrequently forms the white crusts which are nearly pure lime and are locally known as "caliche."

Generally the crusts acquire a specific color different from the colors of the overlying and underlying horizons. More commonly the color is somewhat pinkish brown or reddish brown, rich brownish red, red, or brown, and less frequently it is gray or white. In by far the great majority of cases it is considerably darker than the color of the other horizons in the profile.

The exact origin of the desert crusts in still unknown. Glinka (1) mentioned not less than three theories suggested by different authors as an explanation of their formation; namely, (*a*) relics, (*b*) Solonchak (or evaporation), and (*c*) illuviation.

According to the theory of relics, the hardpan or crusts were formed during the preceding epoch, which was characterized, it is assumed, by a climate different from and presumably more humid than that of the present time. Although it is not made quite clear what influence on the formation of the hardpan is ascribed to the greater humidity, it is evident that the supporters of this theory assume that the existing conditions are not adequate for such a development. It naturally follows that the hardpan as a geological relic has no genetic relationship with the other horizons which may be developed by a general soil-forming process operating under existing conditions. If such be the case, the desert crusts cannot be considered as a true genetic soil horizon of the presently evolving regional profile of the Desert soil, but should be regarded as a peculiar feature of the parent material from which this profile evolves. Moreover, since the natural conditions of crust formation no longer exist, and since the present conditions are not adequate for their development, one should assume that the hardpan must undergo certain gradual changes and ultimately complete destruction by weathering, due to its exposure to the influence of the new and antagonistic conditions.

In some particular cases a theory of geological relics can be applied as an explanation of the hardpan formation in connection with a general evolution of the existing geomorphological landscape. This refers to the hardpans found in the soils of the dry basins of the originally submerged region. It has been mentioned above that in the Pleistocene period a number of the large inland seas and lakes occupied much of the territory of the desert. These lakes occupied the broad relatively flat and closed depressions, some of which are below

sea level, and acted as the basins of accumulation of the salts leached from soils of the surrounding country and carried into them by inflowing streams. With the change to a drier climate the lakes shrunk through evaporation, which naturally was accompanied by a concentration of salts and the formation of the huge deposits of them like those in Death Valley and various other parts of the desert.

In such cases, if they lead to a hardpan formation, the hardpan would appear also as a geological formation developed independently from the influence of the presently operating process of formation of the Desert type of soil. In addition, these particular forms of hardpan should be regarded as a local formation rather than a zonal characteristic of the entire physiographic province.

The theory of evaporation is based on an assumption that the general trend of the desert crust formation is essentially the same as that of the formation of the Solonchak. The Desert crusts are a product of the arid regions characterized by a restricted rainfall and a rather high temperature. A limited amount of precipitation nevertheless is supposed to be sufficient for the leaching of the most readily soluble salts. According to Glinka, such salts as NaCl and even gypsum are leached from the soil by the natural drainage. On the other hand evaporation caused by high temperatures, increased by winds, is sufficiently strong to cause an upward capillary movement of the solutions from the deeper strata. This leads to a rising and progressive accumulation of certain salts near the surface of the soil. The complex of these salts consists of the comparatively more resistant salts, due to the previous leaching of the readily soluble ones. "In this way" according to Glinka (1) "are formed the solid crusts composed of lime carbonates, chemically combined silica, oxides of iron and water with traces of NaCl; these crusts are characterized by a light red, or brownish, or gray or white color."

This theory regards the desert crusts as a product of the existing environment. According to it, the hardpan is a true genetic horizon of an accumulation of certain compounds, which develops in connection with a general evolution of the regional soil profile. The mechanism of the process, or at least its main trend, is similar to that of the Solonchak formation. This naturally suggests a classification of the desert crusts together with the Solonchaks in one great group of the genetically related soils, despite their distinctive morphology and areal distribution. The Solonchaks occur mainly as the intrazonal soils analogous to the intrazonal hydromorphic soils of the more northern and more humid zones. Their development generally, if not typically, is a result of the occurrence of a ground water table comparatively close to the surface. Joffe states (3, p. 438) that the Solonchak "forms where the ground waters come to the surface temporarily or for longer periods of time. With the evaporation and low rainfall the salts crystallize and accumulate at the surface." The Solonchak is known as a soil without any particular arrangement of its profile and without a development of particular and typical horizons.

Especially an absence of a distinct zone of compactness or cementation and of a specific structural arrangement of the soil mass generally is considered a typical feature of true Solonchaks.

As compared with this, even the now available and rather incomplete data regarding the occurrence of the desert crusts suggest that their geographical distribution is of a zonal character. In addition to a striking morphological distinction between the desert crust and the typical Solonchak, there is some difference in their chemistry. Most of the salts of the Solonchaks are of the readily soluble group, whereas the desert crusts in most cases are cemented by the more resistant compounds the translocation and accumulation of which may proceed much more slowly and with greater difficulties. These differences may prove that the desert crusts and the Solonchaks represent two independent types of soil formation, despite a certain similarity in their general mechanism.

The third theory of the desert-crusts formation, designated as a theory of illuviation, has been suggested by the fact that the solid crusts very infrequently are exposed on the surface. Generally they occur at some depth from the surface of the soil and are overlain by a mantle of mellow even loose soil material the thickness of which varies from just a few inches to several feet. Glinka (1) cites the observation of Passarge on the crusts in the desert steppe of Algeria where crusts from 0.5 to 2 m. thick everywhere are covered by a layer of mellow soil from 7.5 to 30 m. thick, and points out: "... if it is so, then a question arises whether in many cases the carbonate crusts do represent an ordinary carbonate illuvial horizon which is common to all soils of the desert steppes."

Hilgard (2, 183–185) also shares the opinion concerning the illuvial origin of the hardpans. He states:

> By "hardpan" is understood a dense and more or less hardened layer in the subsoil ... usually of limited thickness only; the direct consequence of their mode of formation, which is not direct deposition by water or other agencies, but the infiltration of cementing solutions into a pre-existing material, originally quite similar to that of the surface soil. Such solutions usually come from above, more rarely from below, and are of various composition. ... The surface soil being the portion where rock weathering and other soil-forming processes are most active, these solutions are chiefly formed there; and according as their descent into the substrata is unchecked, or is liable to be arrested at some particular level, whether by pre-existing close-grained layers or by the cessation of rains, the subsequent penetration of air, and evaporation of the water alone by shallow-rooted plants, may cause the accumulation of the dissolved matter at a certain level year after year. Finally there is formed a subsoil mass more or less firmly cemented by the dissolved matter, sometimes to the extent of stony hardness. ... The cause of the formation of hardpan is a stoppage of the water in its downward penetration.

The theory of an illuvial origin of the desert crusts apparently regards the solid crust and an overlying mellow mantle as the true genetically bound horizons of a normally developed profile. In order to accept this theory one must assume: (*a*) that the rainfall is or was at some time sufficient for considerable leaching of the desert soils; (*b*) that the upper mellow layer of soil

has been modified into an eluvial horizon; (*c*) that originally this horizon contained the compounds which were gradually dissolved and removed from it by leaching and deposited in the crust, which should be accompanied by a considerable chemical decomposition of the mineral soil in the eluvial horizon; (*d*) that there ought to be a certain balance between the cementing materials accumulated in the crust and their content in the original material of the eluvial horizon; and, finally, (*e*) that this process proceeds to operate at the present time or it has been operating in the past under different climatic conditions. The last assumption naturally would regard the crust as a relic which remains for a certain period of time, practically untouched by the later development, whereas the loose and physically less protected eluvial horizon could undergo certain mechanical changes, which would break the initial genetic bounds between these two horizons established at the time of leaching.

The author's observation of the soils in the Mojave and Colorado Deserts shows that various firmly consolidated crusts (lime, gypsum, or silica) are, in the great majority of cases, covered by a layer of unconsolidated and often loose material. Occasionally the crusts were found exposed on the surface. In most of these cases, however, there were some indications that the loose material has been removed by surface sheet erosion or by wind. The thickness of the unconsolidated mantle varies from just a few inches to several feet; sometimes it is more than ten feet thick, but more commonly it varies from one to three feet. In many places the boundary between the mellow soil and the solid crust is rather abrupt. Not infrequently the material of the mellow mantle shows a finely stratified composition which definitely suggests its deposition and accumulation by the wind drifts, by running water, or by both alternatively. In most cases, however, it does not show any particular arrangement and is composed of unassorted and predominantly coarse-textured, gritty drift. In many places its texture differs from that of the crust in a somewhat lower content of clay, which is especially noticeable when this mantle does not rest on a typical crust but is underlain by a red claypan. Its surface almost everywhere is marked by the rather violent run-off in sheets caused by spontaneous cloudbursts and also by *wind drifts* which produce the typical hummocky microrelief of the desert's surface. No marks of vertical leaching were observed. As a rule this material does not contain any lime, gypsum, or other salts, which, however, may occur in a great quantity below it in the crust. The microrelief of the surface of the crust has no definite relation to the microrelief of the surface of the soil. The material of the mellow layer hardly shows any marks of soil profile development throughout its entire thickness, other than a thin vesicular layer on the surface, which has been mentioned in connection with the desert pavement.

All this leads to a conclusion that a real genetic relationship between the solid crust and the loose or mellow mantle which overlies it is rather doubtful, if possible at all. It is more likely that these two layers are not genetically bound horizons of a harmoniously and normally developed profile. The mate-

rial of the upper layer is of comparatively recent origin; it has been flushed by run-off from the relatively elevated areas spread over the surface, which are often drifted and redeposited by winds; it still does not rest stationary but undergoes casual drifting and redeposition and influx of fresh drifts brought in by sporadic windstorms and cloudbursts. This material does not contain much if any soluble salts which could be leached downward and produce a cementation of the crust. Consequently a formation of the desert crusts, through leaching of the upper and mellow layer of the soil and by illuviation, seems rather improbable, although this does not exclude entirely the possibility of a certain mechanical infiltration of the clay fraction into the deeper part of the loose mantle which may contribute to the formation of the crust.

From our studies of morphology of the Desert soils it appears more likely that a development of the desert crusts is due mostly to an upward capillary movement of the moisture from the deeper strata. The salts carried in these solutions do not reach the surface of the soil, probably because solutions as such do not reach the surface, their water being vaporized before they reach it, and also because of a break in the capillaries due to the sharp change in soil texture. No one particular salt is typical for the desert crusts formation as a zonal characteristic: it may be lime, gypsum, silica, or any other salt which may occur in the rising solutions. The supply of these salts may be provided by the local accumulations of them in the dry basins or by general weathering of various rocks.

It is not improbable, however, that in some particular regions of the desert the crusts of various origin can be found. As strictly local formations, these local crusts are not typical for the Desert type of soil formation in general.

It has been mentioned already that the firm crusts do not occur everywhere throughout the full expanse of the desert. Their development is not a constant characteristic of the Desert type of soil formation in general, although their frequent occurrence in large and widely scattered areas throughout the entire Desert soils zone indicates that they are a zonal formation and a product of this particular type of soil formation, the general trend of which is manifested by the process of their own formation.

Apparently the solid crusts or hardpan develops wherever there is a feeding source of salts and other cementing materials and an environment favorable for a continuous upward capillary movement of the solutions. Naturally they are most spectacularly developed in the regions covered by the thick strata of the unconsolidated drifts and various other loose deposits, whereas, in the regions of shallow endodynamomorphic soils underlain by solid rocks, they may be entirely absent or appear in entirely different forms.

A much more common feature of the residual group of the Desert soils is the development of a certain horizon of relative compactness, which already has been mentioned and described. Because of a relatively higher content of clay in this horizon than in the others, it is commonly designated a "claypan." The reddish claypan is not a feature of the residual Desert soils only: in this or

other forms it occurs in most of these soils, not excluding those with typical desert crusts, and consequently should be regarded as one of the principal zonal characteristics of the Desert type of soil formation.

The claypan in the Desert soils is often spoken of as a result of the "clay migration" or "clay accumulation," which suggests an illuvial origin and nature of this horizon. Accordingly one must assume that the overlying horizon is eluvial in nature, from which the clay has been removed by leaching and shifted into the zone of a claypan formation. Hardly any evidence, other than the difference in texture of these two horizons, can support this interpretation, whereas against it can be repeated the same arguments which were mentioned in a discussion of the illuvial origin of the desert crusts.

The probability may be admitted of a certain mechanical infiltration of the clay into the deeper horizons of the soil, which may contribute to the claypan formation in some particular cases. The main causes of this development, however, seem to differ greatly. A normal development of the soil profile proceeds through a harmonious development of all its horizons. A development of the illuvial horizons cannot be accomplished without a simultaneous development of the eluvial horizons. The latter have morphological characteristics no less distinct than those of the former, although different in nature. Our studies of the Desert soils did not give us any data pointing to the development of eluvial horizons in these soils. This leads us to the conclusion that a steady leaching of the Desert soils is hardly probable. A development of the reddish clayey horizon, designated above as a "claypan" and similar in appearance to the normal illuvial horizons, more likely is a result of hydrolytic decomposition of certain minerals, mainly of feldspars and hornblende *in situ*, their kaolinization, and the subsequent dehydration of the products of decomposition during the hot and dry periods. The feldspars constitute probably the most voluminous ingredient of most crystalline rocks, such as granite gneiss, basalt, diabase, diorite, gabbro, lavas, etc. According to Hilgard (2, p. 32), "The feldspars are decomposed by weathering rather readily, and are important in being the chief source of clay as well as of potash in soils. When acted upon by carbonated water; the bases potash, soda, and lime or carbonates, the silica being mostly displaced; while the silicate of alumina takes up water and forms kaolinite, the essential basis of clays, and one of the most important constituents of soils; imparting to them the necessary firmness and cohesion, together with other important physical properties. . . ." A decomposition of the black hornblende, another important rock ingredient, supplies considerable amounts of the iron hydrates. A process of dehydration leads to the formation of the sesquioxides of the type of turgite and hematite, which give the horizon its conspicuous rather bright reddish color. Joffe (3, p. 83) quotes Glinka and points out: "In the arid climate with high temperature the dehydration effects are well expressed as in the case of the desert regions of Southern California. Glinka cites examples of the red colored desert steppes of Australia, North Africa, and Central Arabia. He ascribes the red color to the presence of turgite, a dehydrated iron oxide."

Hilgard's general and rather theoretical view on this subject differs from ours. He (2, p. 47) made a statement: "Since kaolinization is also a product of hydration, the presence of water must greatly influence its intensity, and especially the subsequent formation of colloidal clay; so that rocks forming clay soils in the region of summer rains may in the arid regions form merely pulverulent soil material." Later on he states (2, p. 163) that in the arid regions "the formation of colloidal clay is very much diminished, so that most soils formed under arid conditions are of a sandy or pulverulent type. There is then little or no clay to be washed down into the subsoil, hence there is no compacting of the latter." Our own observations do not agree with the last statement of Hilgard: we found a horizon of compactness with a content of clay greater than that in the surface soil to be a typical feature of the great majority of the normally developed Desert soils. A similar objection has been made by Lapham (4), who states that "general and early studies of Hilgard and others . . . were directed largely to areas of unweathered or but slightly weathered alluvial soils of the stream valleys. . . ."

We agree with Hilgard that kaolinization does not take place in the surface section of the soil, which generally is composed mainly of the products of a mechanical disintegration of rocks that proceeds in these regions far in advance of their chemical decomposition. We agree also that this may be due to a deficiency of water. Kaolinization proceeds, however, at some distance from the surface of the soil, though at a slower rate here than in the more humid regions. It appears that a more or less loose, not infrequently even pulverulent, consistence of the upper horizons of the soil is one of the causes of this kaolinization at some distance from the surface. Apparently a sufficient amount of moisture from the transient desert rains penetrates the subsoil and, although the surface soil dries and loses its part of the moisture almost as soon as the rain is over, the subsoil retains its part which is protected by the poor capillarity of the overlying material. A conservation of moisture is helped also by the scant vegetation and the comparatively slight transpiration of water from the subsoil by plants. A hydrolytic action, moreover, must be considerably stimulated and intensified by a high temperature, the heat, however, not being great enough to cause rapid vaporization of the moisture.

An assumption that the claypan formation is due to a hydrolytic decomposition of the feldspars, hornblende, and other minerals *in situ* naturally leads to a conclusion that a development of the claypan has no genetic connection with a development of the desert crusts. Each of these two formations has its own and different causes and each can be developed and reach a certain stage of maturity independently from the other. In some particular cases one may observe a soil profile with a strongly developed crust and with practically no traces of the claypan formation. Much more often a soil without a distinct hardpan has a perfectly developed claypan. A majority of the soils with hardpans show more or less clear indications of the simultaneous development of the claypan. In such cases the claypan not infrequently, if not typically, develops just above the crust, and probably the crust itself stimulates

its formation by preserving the moisture above its surface. In a number of other cases a reverse situation has been observed, in which a claypan apparently stimulates the formation of crust. Generally the claypan is comparatively free from an abnormal content of salts; in some instances, however, it appears as a zone of concentration of the salts, probably due to its stimulation of crystallization. Especially often it becomes impregnated with lime. An excellent example of this is provided by the soils of the Mojave and related series. In extreme cases a concentration of lime in these soils leads to the formation of the pure limy crusts (caliche). A crust-producing cementation apparently may overlap the entire zone previously kaolinized, and it is not improbable that the reddish color which characterizes many of the desert crusts is due to a coexistence or a preexistence of kaolinization and dehydration with the accumulation of the cementing compounds. It is not necessary, however, that these two somewhat antagonistic processes operate continuously and simultaneously: the former naturally must progress during the rainy period, especially during the winter seasons and thereafter (dehydration during a summer hot period), whereas the latter operates during the dry and hot periods.

A number of the large tracts of the desert are occupied by the Solonchaks. They are found in the broad dry lake basins and in the valleys of the desert streams, where the ground water comes close to the surface temporarily or continuously (pl. 3, Fig. 1 and 2). Many of these tracts are covered by the crusts of different salts, among which the chlorides and sulfates are the most common. The author failed to find, however, any Solonetz in the desert. A number of Desert soils develop a morphological profile closely resembling that of the Solonetz, although a close examination of these profiles never failed to dissipate all doubt about their real character, which genetically and apparently chemically has nothing in common with true Solonetz.

An absence of the Solonetz formation in the desert, where the Solonchaks are of a rather common occurrence, is in harmony with the remark made by Glinka about a certain antagonism which can be observed between these two soil types. Often they coexist, although wherever one of them begins to dominate all the other soil types, the other tends to disappear from the landscape completely. This may be a consequence of the difference in the general trends of their formation. The Solonchaks are formed by the evaporation of the upward rising solutions, whereas the development of Solonetz is supposed to be a result of the reverse process, or leaching—a process of which no indications have been found in the Desert soils.

GENERAL DISCUSSION

The Desert type of soil formation is a zonal type of the same category to which belong the other great zonal types such as Tundra, Podzol, Chernozem, and Bourozem. The great northern horizontal zone of the Desert soils extends through North America, northern Africa, and central Asia. Geographically

this zone appears even more complete and more expansive than some other horizontal zones, especially if it is compared with the zones of Chernozems or Bourozems.

Because of the exceedingly low biological pressure of the desert, the Desert type of soil formation is characterized by a greatly reduced biochemical activity. The annual bio-pedo-genic cycles of the desert natural complex do not overlap each other, but each individual cycle ends before the following one begins. This prevents a possibility of the formation of humus. The typical Desert soils are almost wholly inorganic or humusless.

As a consequence of an extreme reduction of the constructive activity of the biosphere, the Desert type of soil formation is dominated by a direct influence of the climatic agencies. These, in turn, are dominated by the temperature, because of the restricted amount of rainfall, which reduces the constructive power of the meteoric moisture so far as the development of a normal soil profile is concerned. The Desert type of soil formation is predominantly termogenic and abiotic.

An evolution of the normal profile of the Desert soils is *effected* by an upward capillary movement of the underground moisture and by a concentration of the chemical decomposition of its mineral skeleton at some depth from the surface. The first process leads to the formation of the desert crusts at some distance from the soil surface, and the second is responsible for a development of the claypan horizon. A cementation of the crust can be produced by different salts or compounds which may occur in the rising solutions, and the crusts are formed wherever the compounds capable of causing cementation are present in the solution. The claypan formation in the Desert soils is a result of a hydrolytic decomposition *in situ* of certain minerals, mainly feldspars and hornblende, and of a subsequent dehydration of the products of hydrolysis. This process does not take place on the immediate surface in the desert environment but proceeds at some depth from the surface.

The development of these two processes can coexist in any particular Desert soil, developing their relative intensity by the alternating waves according to the changes of the climatic seasons. Their products not infrequently overlap each other in the soil profile. In either case, a certain part of the surface soil remains practically unaffected by the corresponding developments. This section of the soil profile may be regarded as a passive, or dead, horizon, in which soil moisture undergoes rapid and easy vaporization by the desert heat. The compounds which may be brought up in the rising solutions and the accumulation of which indurates the crust do not enter the dead horizon and do not reach the surface of the soil because of vaporization of the solvent as soon as it reaches the lower limit of this zone. Because of a deficiency of moisture caused by rapid vaporization of the water which may be supplied by rainfall, hydrolytic activity does not develop in the dead horizon. The upper limit of an effective chemical decomposition of the mineral skeleton, however, seems to be somewhat closer to the surface than the upper limit of precipitation of

the crust-cementing compounds. Moreover, a coexistence of the two processes apparently tends to reduce the depressing influence of the dead horizon and consequently to reduce its thickness. An average and normal thickness of the dead horizon of the Desert soils is not certain: in many instances it is mechanically reduced by wind erosion or by the destructive run-off, whereas in many other cases it is greatly enlarged by a deposition of fresh strata of drifts dropped by the same agencies after the crust or a claypan was formed. Because of a mechanical modification, its thickness varies from just a few inches to considerably more than ten feet. The average normal thickness, however, is not far from one or one and a half feet. It is possible to assume an existence of the "fossil" crusts and claypans buried under much thicker deposits of the fresh drift. The dead horizon in many places is covered by an external "protective" crust, with or without an outblown "desert pavement," and this, if present, with or without a "desert tan" or "desert varnish."

Soils of the Desert type of formation are not subject to leaching and do not develop either eluvial or illuvial horizons. Many of them have a zone of lime concentration, but in general this is not a zonal characteristic in the Desert soils. The lime apparently is brought into the zone of concentration, wherever it is present, in the same manner and from the same sources as any other compound which may precipitate from the rising solutions. Therefore the Desert soils as a whole hardly belong to the group of Pedocals. At the same time, they can hardly be classed with the Pedalfers.

Marbut (6), in his scheme for soil classification, established these two groups as the only subdivisions of the highest category of his system, assuming that every normally developed and mature soil should be either a Pedocal or a Pedalfer. The normal Desert soils do not seem to fit into this scheme, although a number of the local Desert soils can be regarded as members of one or the other main group.

We may assume the existence of not less than three broad types of soil formation. These three correspond to the three principal types of vegetation which are mainly responsible for the turnover and pulsation of the biopedogenic cycles. Accordingly the principal types of soil formation may be designated as a woodland type, a grassland type, and a shrubland type. The first type is that including the Podzol and Laterite soils; the second, Chernozem, Chestnut, Brown, etc.; and the third, the Desert and probably the Tundra. Each of these three types is characterized by a particular grade of biological pressure, according to which it may be termed a type of a high, moderate, or low biological pressure, respectively.

The Desert type of soil formation is a shrubland type, or a type of low biological pressure.

REFERENCES

(1) GLINKA, K. D. 1931. Pedology (Pochvovedenie). Fourth post mortem edition (in Russian), pp. 439–444.

(2) HILGARD, E. W. 1906. Soils. The MacMillan Co., New York.
(3) JOFFE, J. S. 1936. Pedology. Rutgers University Press, New Brunswick, N. J.
(4) LAPHAM, M. H. 1932. Genesis and morphology of desert soils. *Amer. Soil Survey Assoc. Bul.* 13: 50.
(5) MARBUT, C. F.—Soils of the United States. *Atlas of American Agriculture*, part III: 81.
(6) MARBUT, C. F. 1927. A scheme for soil classification. *Proc. First Internat. Cong. Soil Sci.* 1927: 19.
(7) MERRILL, C. P. 1904. Rocks, Rock Weathering and Soils, p. 256. The MacMillan Co., New York.

PLATE 1

FIG. 1. Characteristic erosion of the mountain slopes of the Desert region.

FIG. 2. The head of an alluvial fan covered with freshly deposited drift.

FIG. 3. Characteristic erosion of the mountain ranges and formation of the alluvial fans.

FIG. 4. Two typical landscapes of the Desert: mountain ranges and gently sloping intermountain plains.

FIG. 3

FIG. 4

FIG. 1

FIG. 2

PLATE 2

FIG. 1. Spring flora of the Mojave Desert. April, 1935.

FIG. 2. Typical vegetation of the Mojave Desert in the summer dry period. A bare inter-shrub area covered with desert pavement.

FIG. 3. Creosote bushes, the most typical shrub of the southern Desert.

FIG. 4. Sagebrush of the Mojave Desert.

FIG. 3

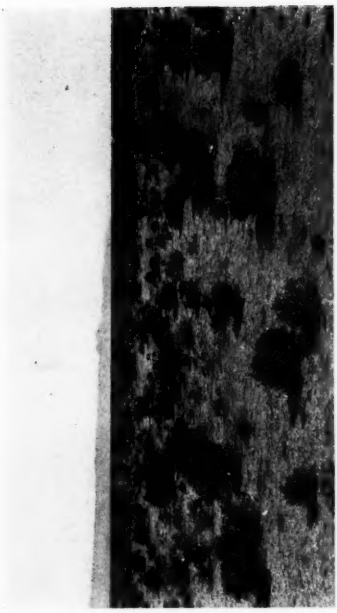

FIG. 4

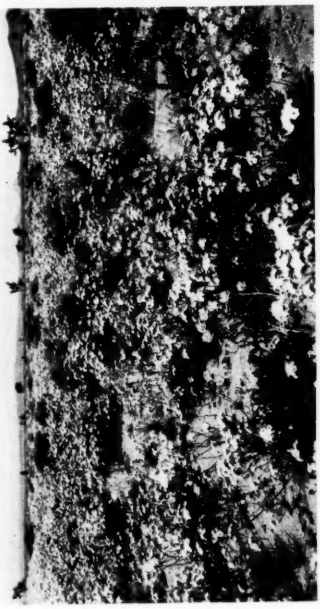

FIG. 1

FIG. 2

PLATE 3

FIG. 1. Solonchak area in the valley of Mojave River, east of Barstow.
FIG. 2. Wet Solonchaks in the valley of the Mojave River.
FIG. 3. Salt deposits on the floor of Death Valley.
FIG. 4. Desert's vegetation. Giant cacti in southwestern Arizona.

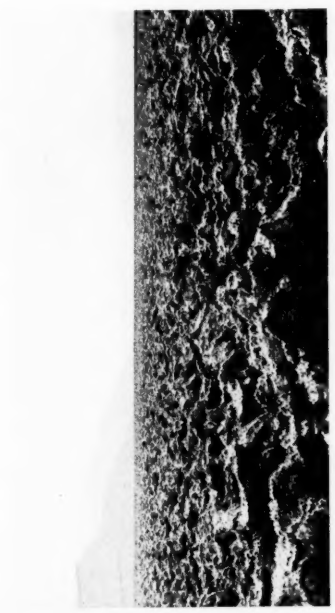

FIG. 3

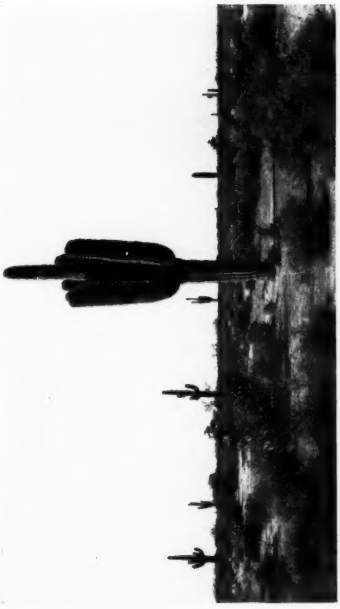

FIG. 4

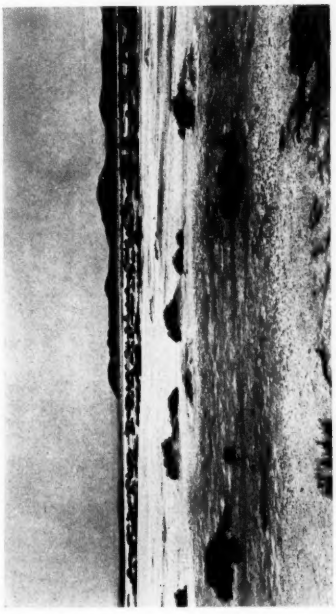

FIG. 1

FIG. 2

EFFECT OF CALCIUM CYANAMIDE[1] ON THE SOIL MICROFLORA WITH SPECIAL REFERENCE TO CERTAIN PLANT PARASITES[2]

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Calcium cyanamide, when applied in sufficient quantity, has a marked influence on the microflora and the fauna of the soil. The effects on the organisms may be either stimulative or depressive in nature and seem to be determined to a considerable extent by the soil reaction, the soil type, the quantity of calcium cyanamide applied, and the specific organism involved.

Several authors (1, 13, 25) have reported marked changes in the bacterial flora of the soil, following applications of calcium cyanamide. Under certain conditions (13, 25), a partial sterilization of the soil occurred, resulting in a very marked decrease in the bacterial population for several days after the calcium cyanamide was added. After this brief period of depression, the number of bacteria increased very rapidly for a time and then gradually returned to normal.

Less is known about the effect of calcium cyanamide on the fungous flora of the soil. There is evidence, however, that the abundance and activity of the soil fungi may be influenced greatly by applications of calcium cyanamide, and in a few cases this material has exhibited sufficient fungicidal action to suggest its use as a possible control agent for specific plant diseases. Promising results have been reported, for example, on the control of club-root of crucifers caused by *Plasmodiophora brassicae* (11, 18, 19, 21). A fungous disease of chestnut caused by *Blepharospora cambivora* (17), a root rot of pan (Papaver) caused by *Phytophthora parasitica* (4), downy mildew of hops (8), a black root rot of radish caused by *Aphanomyces raphani* (2), and seed decay and damping-off of seedlings (5, 12) have also been partially controlled by the addition of calcium cyanamide to the soil.

A toxic action of calcium cyanamide on certain injurious worms and larvae in the soil has also been observed by numerous workers. It has also been

[1] The calcium cyanamide used in these experiments was a commercial product containing approximately 61.5 per cent $CaCN_2$, 17.5 per cent $Ca(OH)_2$, 11.5 per cent C, and 9.5 per cent miscellaneous substances. Rates of application expressed in pounds of calcium cyanamide per acre refer to pounds of the commercial product and not to pounds of $CaCN_2$.

[2] Journal Series paper of the New Jersey Agricultural Experiment Station, department of plant pathology.

used, with more or less success, as a control for certain plant-parasitic nematodes (3, 6, 10, 14, 20, 22, 23, 24) and has been found to have a toxic action on wire worms (16), house-fly larvae (9), and white grubs (15).

These few references do not cover completely the literature on this subject but are sufficient to show that calcium cyanamide has a definite effect on the microorganisms and fauna of the soil.

The experiments here reported were designed to obtain additional information on the effect of calcium cyanamide on the bacterial and fungous flora of the soil, with special reference to plant pathogenes. A study was first made of the effect of various rates of application on the general soil microflora, expressed in numbers of bacteria, actinomyces, and fungi, as determined by the plating method. Another group of experiments was conducted to study the effect on specific soil-borne, plant-parasitic fungi, using incidence of disease as an index to the activity of the parasite. The parasites considered were *Plasmodiophora brassicae* (club-root of crucifers), *Rhizoctonia* and *Pythium* (seed decay and damping-off of seedlings), *Aphanomyces euteiches* (pea root rot) and *Actinomyces scabies* (beet scab). Major attention was given to *Plasmodiophora* and the damping-off fungi.

EFFECT OF CALCIUM CYANAMIDE ON THE GENERAL SOIL MICROFLORA

Two soils differing widely in pH reaction were used in the study of the effect of calcium cyanamide on the number of bacteria and fungi in the soil as determined by the plating method.

The soil used in the first experiment was a fertile Sassafras loam with an initial pH value of 4.5. Immediately after the soil was brought from the field, it was screened; weighed amounts were placed in 2-gallon glazed earthenware pots, and calcium cyanamide was added. The rates of application of calcium cyanamide per acre, calculated on a 6-inch-acre, soil-volume basis, are given in table 1. The soil of each pot was thoroughly mixed after the calcium cyanamide treatment and again before samples were taken for each of the several platings. All treatments were made in duplicate. The moisture of the soil in each pot was maintained, by readjustment every other day, at a point considered favorable for the development of microorganisms.

Soil samples for bacterial and fungous plating were taken from each pot on the third, tenth, thirtieth, and sixtieth days after treatment. Five dilution plates from each sample were poured with Waksman's peptone-glucose acid agar adjusted to pH 4 for fungous counts, and five others with Waksman's sodium albuminate agar adjusted to pH 7.2 for counts of bacteria and actinomyces. Each count recorded is the average of ten plates poured from each treatment.

The pH at each sampling was determined by the colorimetric method, $BaSO_4$ being used to clear the suspension.

The second experiment was conducted with a Sassafras loam soil similar

to that used in the first test, but the initial pH in this case was 6.5. This test included only an untreated series and a 2,000-pound-per-acre treatment with calcium cyanamide. Otherwise, the methods used were like those employed in the first experiment.

The results of these two experiments are presented in tables 1 and 2.

It will be seen that, in the acid soil, the development of bacteria and actinomyces was, with one exception, accelerated up to the 30-day period by the application of calcium cyanamide. The 10,000-pound-per-acre application

TABLE 1

Effect of calcium cyanamide on soil reaction and on numbers of microörganisms in a Sassafras loam soil with an initial pH of 4.5

ACRE APPLICATION OF CYANAMIDE	REACTION			BACTERIA				ACTINOMYCES				FUNGI			
	10 days	30 days	60 days	3 days	10 days	30 days	60 days	3 days	10 days	30 days	60 days	3 days	10 days	30 days	60 days
lbs.	*pH*	*pH*	*pH*	*m.p. gm.**	*m.p. gm.*	*m.p. gm.*	*m.p. gm.*	*100t. p.gm.†*	*100t. p.gm.*	*100t. p.gm.*	*100t. p.gm.*	*t.p. gm.‡*	*t.p. gm.*	*t.p. gm.*	*t.p. gm.*
0	4.5	4.5	4.5	7	13	5	2	9	15	18	8	99	138	247	223
80	4.7	4.6	4.6	5	10	11	2	10	21	26	6	110	196	297	354
400	5.0	4.7	4.7	6	11	8	2	14	22	26	5	114	247	272	248
2,000	6.6	6.0	4.8	14	16	24	2	15	16	42	11	92	199	208	208
10,000	8.6	8.6	8.4	16	88	462	31	30	171	964	81	0	0	0	3

* Millions per gram.

† 100-thousands per gram.

‡ Thousands per gram.

TABLE 2

Effect of calcium cyanamide on soil reaction and on numbers of microörganisms in a Sassafras loam soil with an initial pH of 6.5

ACRE APPLICATION OF CYANAMIDE	REACTION			BACTERIA			ACTINOMYCES			FUNGI		
	1 day	10 days	30 days	1 day	10 days	30 days	1 day	10 days	30 days	1 day	10 days	30 days
lbs.	*pH*	*pH*	*pH*	*m.p. gm.*	*m.p. gm.*	*m.p. gm.*	*100t. p.gm.*	*100t. p.gm.*	*100t. p.gm.*	*t.p. gm.*	*t.p. gm.*	*t. p. gm.*
0	6.5	6.5	6.5	7	6	4	4	5	4	18	26	12
2,000	8.4	8.4	8.0	4	39	56	5	20	52	13	1	1

was especially effective in this respect, showing approximately 92 times as many bacteria and 53 times as many actinomyces in the treated as in the untreated soils, 30 days after the calcium cyanamide was applied. At the 60-day period, the soils which received the 10,000-pound application of calcium cyanamide still showed a much larger number of bacteria and actinomyces than did the untreated soil, but the number was rapidly returning to normal.

The fungi showed a slight increase in number in soils which received 80 and 400 pounds of calcium cyanamide per acre, respectively, but there was a de-

cided reduction in number where heavier applications were made. In the 2,000-pound application, the counts did not differ appreciably from those obtained from the untreated soil, but in the 10,000-pound-per-acre treatment, no fungi were found until 60 days after treatment, and then only a few.

In the second test, where the initial soil pH was 6.5, the effects of the calcium cyanamide treatments were more marked. The 2,000-pound-per-acre application caused a much greater increase in bacteria and actinomyces and a greater decrease in fungi in this soil than did the same amount in the more acid soil. This would seem to indicate that the effect of the calcium cyanamide on the microflora of the soil is influenced to a marked degree by the initial pH value of the soil.

It will be observed that, in both the acid and the near-neutral soil, the marked change in bacterial and fungous counts occurred in those treatments which raised the pH values well above the neutral point, indicating that the soil reaction may be of greater significance than the amount of material used.

EFFECT OF CALCIUM CYANAMIDE ON SPECIFIC SOIL-BORNE PLANT PATHOGENES

Studies on the effect of calcium cyanamide, used alone and in combination with lime, on club-root of crucifers (*Plasmodiophora brassicae*) were conducted both in the greenhouse and under field conditions. The greenhouse studies were conducted with two lots of Sassafras loam naturally infested with *Plasmodiophora brassicae* and showing initial reactions of pH 4.6 and 6.4, respectively. The more acid soil was taken from a plot which had not been limed recently. The less acid lot came from an adjacent plot which had received lime in each of the four previous seasons.

The soils were screened and placed in 1-gallon glazed earthenware pots. Calcium cyanamide and hydrated lime were applied at various rates per 2,000,000-pound acre and thoroughly mixed with the soil. Three pots were used for each treatment. The pots were seeded to rape one week after treatment and were maintained at a soil moisture and temperature favorable for the development of club-root.

On the acid series, three consecutive crops of rape plants were grown. The first was seeded June 3 and harvested July 3. The second crop, planted in the same pots without further treatment, was seeded July 20 and harvested August 20. The third crop consisted of healthy young plants set into the pots on August 20. In the less acid series, only one crop was grown. This was seeded June 3 and harvested July 3.

The results are presented in table 3. It will be observed that 1,600 pounds of calcium cyanamide per acre gave almost perfect control of club-root in both the acid and the near-neutral soils. The 800-pound application gave only slight control on the first crop of seedlings in the acid soil, whereas a somewhat better, though not complete, control was obtained on the less acid soil.

Applications of 400 pounds or less per acre had no apparent effect on club-root infection in the more acid soil on the crop planted 1 week after treatment. Slight control was obtained from these same treatments on crops planted 1 and 2 months later. In the near-neutral soil, the 400- and 200-pound applications gave 10.7 and 16.3 per cent infected plants, respectively, as compared with 51.4 per cent for the untreated series.

Compared with hydrated lime, the calcium cyanamide showed a somewhat greater controlling action, pound for pound, 1 unit of calcium cyanamide giving approximately the same results as 2½ units of hydrated lime. This was

TABLE 3

Comparison of efficiency of calcium cyanamide and hydrated lime for control of club-root on rape grown in pots

SOIL TREATMENT	ACRE APPLICATION	CLUBBED PLANTS ON SOIL PREVIOUSLY UNLIMED, INITIAL pH 4.6				CLUBBED PLANTS ON SOIL PREVIOUSLY LIMED, INITIAL pH 6.4	
		Soil reaction	First crop	Second crop*	Third crop*	Soil reaction	First crop
	lbs.	*pH*	*per cent*	*per cent*	*per cent*	*pH*	*per cent*
Check	0	4.6	99.7	82.7	100.0	6.4	51.4
Lime	500	5.4	100.0	72.8	100.0	6.7	16.7
Lime	1,000	6.0	100.0	57.3	78.6	7.0	7.5
Lime	2,000	6.6	96.9	21.4	66.7	7.6	2.5
Lime	4,000	7.3	36.4	2.4	6.7	...	....
Lime	8,000	8.4	2.3	0	0	...	....
Cyanamide	100	4.7	100.0	63.9	86.7	...	....
Cyanamide	200	4.8	100.0	47.0	93.3	6.5	16.3
Cyanamide	400	5.0	100.0	59.0	80.0	6.6	10.7
Cyanamide	800	5.5	91.6	17.7	73.3	6.7	7.5
Cyanamide	1,600	6.5	1.9	0	20.0	6.8	0

* No further treatment.

particularly true shortly after treatment. Both hydrated lime and calcium cyanamide proved more effective as club-root control agents in soils with relatively high pH values.

A more extensive study of the effect of calcium cyanamide on club-root was made under field conditions. Calcium cyanamide and hydrated lime were used in two testes with rape grown on a Sassafras loam soil naturally infested with *Plasmodiophora brassicae*. The first experiment was started in 1932 and continued through 1933 and 1934. The second was conducted in 1934 only. In each case, a ½-acre lot was divided into twelve square plots, $\frac{1}{24}$-acre in size. The materials were applied broadcast after plowing and were disced or rototilled into the soil to a depth of 4 to 5 inches. Rape was planted in drills 24 inches apart and cultivated several times, thus giving ample opportunity for reinfestation of treated plots from adjacent untreated ones. Five treatments

and a check, each run in duplicate, were used in each experiment. When the largest plants were approximately 24 inches high, data were obtained on the green-weight yields and on the percentage and severity of club-root infection.

In 1932, the stand of rape in the experimental plots was very irregular because of a prolonged drought following seeding. Consequently, no yield records were taken for that crop. Data were obtained, however, on the height of plants and on the percentage of club-root infection.

For each of the other crops, yield data were obtained by cutting and immediately weighing the plants in a representative 10-foot length in each of six rows in each plot. After the above-ground parts had been harvested and weighed, all the roots from the harvested plants were carefully removed and examined for club-root infection.

Tables 4 and 5 give the annual soil treatments and the results obtained in the two experiments.

It will be seen that in the 3-year experiment (table 4) 600 pounds of calcium cyanamide, applied annually, had little or no effect on club-root. On the other hand, three annual applications of 1,200 pounds reduced the amount of infection appreciably, although one plot receiving this treatment still showed 73 per cent infected plants in the third season. The 1,200-pound application of calcium cyanamide showed a good increase in yield in both 1933 and 1934, however, despite the high percentage of clubbed plants. On these plots infection was retarded and reduced in severity, which allowed the development of numerous feeding roots even on severely clubbed plants.

Plots which received hydrated lime only, applied at the rate of 3,000 pounds per acre in 1932 and 1933 and of 1,500 pounds per acre in 1934, gave, from the standpoint of plant growth, what appeared to be excellent club-root control in 1933 and 1934. Root examinations, however, showed as high as 45 per cent infection in 1933 and 37 per cent in 1934. It is of interest to note that the soil reaction on these plots at harvest time was 7.3 to 7.6, or above the point where club-root development usually occurs.

Plots which received hydrated lime alone, applied at the rate of 6,000 pounds per acre in 1932 and 1933 and of 3,000 pounds in 1934, showed what appeared to be perfect club-root control, as far as above-ground effects were concerned. Severe clubbing of the roots was also practically eliminated on these plots. It is significant, however, that even here there was still 11 to 16 per cent club-root in 1933, despite the high pH (pH 7.6 to 7.7).

Plots which received a total of 7,500 pounds of hydrated lime and 1,800 pounds of calcium cyanamide (table 4) during the 3-year period showed much better control than did plots receiving 7,500 pounds of lime alone or 1,800 pounds of calcium cyanamide alone. Over the 3-year period this combined treatment with calcium cyanamide and lime gave better club-root control than did double the amount of calcium cyanamide used alone, and gave higher yields, though slightly poorer control, than did double the amount of lime used

TABLE 4

Effect of three annual applications of calcium cyanamide, hydrated lime, and a combination of the two on severity of club root, and on yield, of rape

SOIL TREATMENT	ACRE APPLICATION			1932 CROP				1933 CROP					1934 CROP				
	1932	1933	1934	Height of plants	Severely clubbed	Slightly clubbed	Total clubbed	Soil reaction, July 21	Acre yield (green weight)	Severely clubbed	Slightly clubbed	Total clubbed	Soil reaction, July 31	Acre yield (green weight)	Severely clubbed	Slightly clubbed	Total clubbed
	lbs.	*lbs.*	*lbs.*	*inches*	*per cent*	*per cent*	*per cent*	*pH*	*tons*	*per cent*	*per cent*	*per cent*	*pH*	*tons*	*per cent*	*per cent*	*per cent*
Check	0	0	0	14	71	28	99	5.2	10.91	14	56	70	5.1	2.83	86	7	93
Check	0	0	0	14	80	20	100	5.4	7.15	61	38	99	5.4	1.05	100	0	100
Cyanamide	600	600	600	24	81	19	100	5.4	13.61	9	68	77	5.5	3.92	90	6	96
Cyanamide	600	600	600	24	83	17	100	5.7	9.40	71	27	98	5.7	2.25	97	1	98
Cyanamide	1,200	1,200	1,200	20	0	22	22	5.9	17.35	3	35	38	6.2	10.89	22	29	51
Cyanamide	1,200	1,200	1,200	22	34	50	84	5.9	16.92	8	70	78	6.0	9.11	49	24	73
Cyanamide	600	600	600	24	13	43	56	7.6	14.70	1	22	23	7.5	11.69	4	19	23
Lime	3,000	3,000	1,500														
Cyanamide	600	600	600	25	34	53	87	7.6	16.73	2	13	15	7.5	14.45	6	25	31
Lime	3,000	3,000	1,500														
Lime	6,000	6,000	3,000	24	35	40	75	7.6	10.49	0	11	11	7.8	10.60	1	2	3
Lime	6,000	6,000	3,000	26	26	37	63	7.7	12.34	0	16	16	7.7	13.00	0	1	1
Lime	3,000	3,000	1,500	24	55	38	93	7.6	11.83	1	29	30	7.3	10.79	21	16	37
Lime	3,000	3,000	1,500	26	42	40	82	7.6	13.50	5	40	45	7.6	12.92	3	14	17

alone. It would seem, therefore, that the combined action of hydrated lime and calcium cyanamide may be better from the standpoint of both club-root control and crop yield than when either is used alone.

The 1-year field experiment (table 5) was planned to test the effect of heavier applications of calcium cyanamide than were used in the 3-year test. The treatments used, the soil reactions at harvest time, the crop yield in tons green-weight per acre, and the club-root data for this experiment are presented in table 5.

The heavy applications of calcium cyanamide delayed and reduced germination, but the reduced stand on these plots gave a more luxuriant individual plant growth than was obtained on the other plots. The yield records are, therefore, not in proportion to the relative stand obtained.

TABLE 5

Effect of one application of calcium cyanamide, hydrated lime, or a combination of the two on severity of club root, and on yield, of rape

SOIL TREATMENT	ACRE APPLICATION	SOIL REACTION	ACRE YIELD (GREEN WEIGHT)	SEVERELY CLUBBED	SLIGHTLY CLUBBED	TOTAL CLUBBED
	lbs.	*pH*	*tons*	*per cent*	*per cent*	*per cent*
Check	0	5.0	3.60	87	4	91
Check	0	5.3	4.50	91	7	98
Cyanamide	1,200	5.7	8.82	31	31	62
Cyanamide	1,200	6.2	13.94	23	32	55
Cyanamide	1,800	6.0	12.56	35	35	70
Cyanamide	1,800	6.7	7.30	3	25	28
Cyanamide	1,200					
Lime	3,000	6.9	8.78	28	30	58
Cyanamide	1,200					
Lime	3,000	7.0	11.94	3	24	27
Lime	3,000	6.5	6.50	56	24	80
Lime	3,000	7.3	12.96	5	21	26
Lime	6,000	7.1	12.85	9	35	44
Lime	6,000	7.1	10.67	27	42	69

In this experiment, 1,200 pounds of calcium cyanamide per acre reduced club-root approximately 30 to 40 per cent and increased the yield two- to three-fold. The highest yield, 13.94 tons green-weight per acre, was obtained from one of the plots which received 1,200 pounds of calcium cyanamide per acre. Club-root infection on this plot was 55 per cent, with 23 per cent severely clubbed. Despite this clubbing, the plants grew vigorously and showed little ill effects from the disease. The 1,800-pound treatment also gave fair results on one plot, but on the duplicate, the germination was so poor, as a result of cyanamide injury, that the benefits derived from club-root control were largely nullified by the reduction in stand.

The 3,000-pound-per-acre application of hydrated lime gave very poor control on one plot where the treatment raised the soil reaction to only pH 6.5, whereas on the duplicate plot, where the soil reaction at harvest was pH 7.3, club-root control and crop yield were good.

The plots which received 6,000 pounds of hydrated lime per acre showed a reaction of pH 7.1 at harvest time and yielded a crop which, above-ground, seemed to be healthy. Root examination on one plot, however, showed 69 per cent clubbed plants with 27 per cent severely clubbed. Plant growth was not appreciably affected by the disease on these plots, and yields were excellent.

The plots which received 1,200 pounds of calcium cyanamide and 3,000 pounds of lime showed slightly better club-root control than did those on which 1,200 pounds of calcium cyanamide or 3,000 pounds of lime was used alone, but showed no marked increase in yield over the single treatments.

An interesting feature of this test was the marked differences in incidence of the disease and in yield on duplicate plots. Similar irregularities were also observed in the 3-year test (table 4), as well as in a 7-year lime test, which is not recorded in this paper. It seems that small differences in soil humidity, soil reaction, soil type, and possibly other environmental factors within the experimental area determine to what extent a given amount of lime or calcium cyanamide may influence the amount of infection or the relative injury caused by infection. It will also be observed from the tables that the yields obtained are by no means proportional to the percentage of infection. This is due to the fact that, in many cases, severely clubbed plants still have sufficient fibrous rootlets to support a vigorous growth. This condition occurred on many of the severely clubbed plants in the treated plots. On the untreated plots, however, there were few or no fibrous rootlets where plants showed severe clubbing.

EFFECT OF CALCIUM CYANAMIDE ON SEED DECAY AND DAMPING-OFF CAUSED BY PYTHIUM AND RHIZOCTONIA

Two pot tests were conducted with cucumbers planted on a Sassafras loam soil naturally infested with *Pythium* and *Rhizoctonia*. In the first test, calcium cyanamide was thoroughly mixed throughout the soil at rates of 500, 1,000, and 1,500 pounds per acre (2,000,000 pounds). Immediately after treatment, each pot was planted with 15 cucumber seeds. The second series was conducted in like manner, except that the calcium cyanamide was used at rates of 400, 800, and 1,200 pounds per acre. Three half-gallon pots were used for each treatment; and three with untreated soil, as checks.

After the plants were beyond the age at which damping-off is apt to occur, they were removed and another crop was planted without further treatment of the soil. In the second crop of the second series, only the 1,200-pound treatments and the checks were used.

The results are presented in table 6. The calcium cyanamide greatly increased the stand of the first crop in both series, and the 1,000- to 1,500-pound-per-acre applications continued this protective action to the second crop planted 3 weeks after treatment. The 1,000-pound application caused a 2-day retardation, and the 1,500-pound application a 3-day retardation in germination in the first crop, but no ill effects were apparent on the second crop.

Two other pot tests, using both calcium cyanamide and lime, were conducted with a Sassafras soil heavily inoculated with a pure culture of *Rhizoctonia*. The inoculated soil was placed in half-gallon glazed earthenware pots, and

TABLE 6

Effect of calcium cyanamide on seed decay and post-emergence damping-off of cucumbers

ACRE APPLICATION OF CALCIUM CYANAMIDE	TOTAL NUMBER OF SEEDLINGS OBTAINED AND NUMBER REMAINING STANDING AFTER DAMPING-OFF PERIOD			
	First crop		Second crop	
	Germinated	Healthy*	Germinated	Healthy*
lbs.	*per cent*	*per cent*	*per cent*	*per cent*
		Series A		
0	24	17	36	36
500	84	73	36	34
1,000	82	82	62	53
1,500	78	78	64	64
		Series B		
0	20	2	15	11
400	44	15	..	..
800	42	27	..	..
1,200	47	44	67	60

* Based on number of seeds planted.

Series A: First crop planted January 15, harvested February 7, 1932. Second crop planted February 7, harvested February 28. *Series B:* First crop planted December 23, 1932, harvested January 10, 1933. Second crop planted January 10, harvested January 31 1933. Three pots with 15 seeds each, or total of 45 seeds, used for each treatment.

calcium cyanamide and lime were applied at various rates calculated on the basis of 2,000,000 pounds of soil per acre. One week after treatment, the pots were planted with 16 cucumber seeds per pot. Three pots, or a total of 48 seeds, were used for each treatment.

The first crop of seedlings was harvested 3 weeks after planting, or as soon as damping-off ceased; a second planting was made without further treatment of the soil. Data were taken on the total number of seedlings emerged and the number remaining after the damping-off period.

The amounts of calcium cyanamide and lime used and the effects on seed decay and on damping-off of emerged seedlings (post-emergence damping-off)

are presented in table 7. It will be noted in series A where an 800-pound application of calcium cyanamide was made, that there was no beneficial

TABLE 7

Effect of calcium cyanamide and hydrated lime on seed decay and damping-off of cucumbers due to Rhizoctonia

ACRE APPLICATION		SOIL REACTION	TOTAL NUMBER OF SEEDLINGS OBTAINED AND NUMBER REMAINING STANDING AFTER DAMPING-OFF PERIOD			
			First crop		Second crop	
Calcium cyanamide	Hydrated lime		Germinated	Healthy*	Germinated	Healthy*
lbs.	*lbs.*	*pH*	*per cent*	*per cent*	*per cent*	*per cent*
			Series A			
0	0	5.7	62.5	60.4	52.1	41.7
0	3,000	7.5	72.9	66.7	56.2	52.1
800	0	6.4	68.7	60.4	29.2	22.9
800	2,000	7.6	93.7	93.7	72.9	68.7
1,200	0	6.7	93.7	85.4	54.2	41.7
1,200	2,000	8.2	93.7	93.7	81.2	81.2
1,600	0	7.0	93.7	93.7	77.1	68.7
1,600	2,000	8.5	95.8	93.7	95.8	87.5
2,000	0	7.4	97.9	97.9	95.8	93.7
2,000	2,000	8.5+	97.9	97.9	95.8	95.8
			Series B			
0	0	5.70	33.3	27.1	10.4	8.3
0	500	6.00	37.5	27.1	10.4	10.4
0	1,000	6.35	20.8	16.7	14.6	8.3
0	2,000	6.75	37.5	35.4	16.7	12.5
400	0	6.10	50.0	37.5	10.4	10.4
400	500	6.40	43.7	35.4	8.3	6.2
400	1,000	6.80	14.6	12.5	16.7	12.5
400	2,000	7.40	29.2	25.0	18.7	18.7
800	0	6.45	16.7	10.4	35.4	29.2
800	500	6.75	16.7	12.5	43.7	41.7
800	1,000	7.50	12.5	8.3	35.4	33.3
800	2,000	7.80	22.9	12.5	43.7	41.7
1,200	0	6.80	87.5	85.4	81.2	81.2
1,200	500	7.50	89.6	89.6	79.2	70.8
1,200	1,000	7.70	79.2	79.2	81.2	72.9
1,200	2,000	8.10	91.7	91.7	93.7	93.7

* Based on number of seeds planted.

effect on the first crop and that, for some unknown reason, an increase in seed decay occurred in the second crop.

Where 1,200 to 2,000 pounds of calcium cyanamide were used per acre, germination was 94 to 98 per cent in the first crop as compared with 62 per

cent where no treatment was used. With the 2,000-pound application, this protection carried over to the second planting made one month after treatment.

There was slight retardation in germination where the higher quantities of calcium cyanamide were used, but the plants looked normal after emergence. In most cases where 2,000 pounds of lime per acre were used in addition to the calcium cyanamide, seed decay was reduced slightly more than where the cyanamide was used alone.

TABLE 8

Effect of calcium cyanamide on seed decay and damping-off of cucumbers planted immediately after application in drill row

ACRE APPLICATION OF CALCIUM CYANAMIDE	TOTAL GERMINATION AND HEALTHY PLANTS REMAINING AFTER DAMPING-OFF PERIOD		DELAY IN GERMINATION
	Germination	Healthy plants*	
lbs.	*per cent*	*per cent*	*days*
	Series A		
0	32.3	28.0	..
50	84.0	83.7	4
	Series B		
0	74.3	74.3	..
20	90.7	90.7	1
30	91.0	91.0	3
40	83.3	83.3	4
50	73.7	73.7	6
	Series C		
0	41.3	37.3	..
5	48.3	45.0	0
10	66.0	64.0	0
15	83.3	82.7	0
20	85.3	85.3	0
30	85.7	85.7	1

* Based on number of seeds planted.

Series A: Planted January 18; harvested February 4, 1932. Series B: Planted February 6; harvested March 3, 1932. Series C: Planted March 9; harvested March 26, 1932.

In series B (table 7), it will be seen that the results are somewhat erratic for the 400- and 800-pound-per-acre applications; but where 1,200 pounds of calcium cyanamide were used, seed decay was practically eliminated and post-emergence damping-off was reduced to a minimum. The second planting, made one month after treatment, showed a stand of 71 to 94 per cent in the pots which received 1,200 pounds of calcium cyanamide, compared with a stand of 8 to 12 per cent in the pots which received no cyanamide (plate 1).

In this test, the addition of lime in various amounts failed to show the marked influence that was shown in series A (table 7).

Several other experiments were conducted in ground-beds in the greenhouse. Uniform row trenches, 4 inches wide and 2 inches deep, were made by removing a measured amount of soil. Calcium cyanamide was then thoroughly mixed with this removed soil in quantities calculated to make the required rate of application. One-half of the soil-cyanamide mixture was replaced in the trench and pressed down evenly and firmly with a 4-inch board. Cucumber seeds were then carefully staggered in two parallel lines at the rate of 25 seeds to each linear foot, and the remainder of the calcium cyanamide-treated soil was placed over the seed. This method would correspond to a row application of calcium cyanamide in which the material is thoroughly mixed with the soil in the furrow to a depth of 2 inches, seed being planted immediately in this cyanamide-soil mixture.

The calcium cyanamide was used at rates of 5 to 50 pounds per acre, based on rows 30 inches apart. For each treatment, 300 seeds, planted in six replicated rows of 50 seeds each, were used.

The percentage of germination and the amount of post-emergence damping-off are indicated in table 8. It will be observed (table 8 C) that calcium cyanamide applied by this method at rates of 15 to 30 pounds per acre gave 83 to 86 per cent healthy seedlings as compared with 37 per cent where no calcium cyanamide was used. In the 20- to 30-pound applications, seedling emergence was delayed 1 to 3 days, but no permanent injury was observed in these cases. The 40- and 50-pound applications (table 8 A, B) caused serious delay in germination and a stunted, abnormal growth.

It would seem from these data that the fungi which cause seed decay and damping-off in cucumbers may be slightly more sensitive to cyanamide than are the seeds. As a consequence, the fungi may be prevented from developing until the seedlings are past the danger of infection. The margin of safety between the point of protection and the point of injury, however, seems to be very narrow when seeds are planted immediately after application of the cyanamide.

EFFECT OF CALCIUM CYANAMIDE ON APHANOMYCES ROOT ROT OF PEAS

It has been previously reported (7) that certain chemical fertilizers have a tendency to reduce the severity of root rot of peas under both greenhouse and field conditions and that inorganic nitrogen and potash fractions of mixed fertilizers seem to be more effective in this respect than is superphosphate. A pot test, conducted under greenhouse conditions, was set up to compare calcium cyanamide with other nitrogenous fertilizer materials as a controlling agent for this disease. A naturally infested field soil was used. This was placed in gallon pots, with four pots of six plants each for each treatment. The fertilizers were calculated on the basis of surface area and were thoroughly

mixed throughout the pot to a depth of 6 inches. The peas were planted 1 day after treatment. The materials and quantities used and the effect of the treatments on root rot are shown in table 9.

Calcium cyanamide, used at the rate to supply 50 to 100 pounds of nitrogen per acre, gave no control; when used at a rate to supply 200 pounds of nitrogen per acre, infection was reduced appreciably. Calcium cyanamide showed approximately the same controlling action as equivalent amounts of nitrogen in the form of nitrate of soda. Equivalent amounts of nitrogen in the form of sulfate of ammonia gave somewhat better control. A mixed fertilizer, containing one-half its nitrogen as sulfate of ammonia and one-half as nitrate of

TABLE 9

Effect of calcium cyanamide and other nitrogenous fertilizers on the control of root rot of peas caused by Aphanomyces euteiches

SOURCE OF NITROGEN	ACRE APPLICATION	NITROGEN PER ACRE	PLANTS INFECTED
	pounds	*pounds*	*per cent*
None	.....	...	92
Calcium cyanamide	227	50	96
Calcium cyanamide	454	100	92
Calcium cyanamide	681	150	83
Calcium cyanamide	908	200	37
Nitrate of soda	312	50	67
Nitrate of soda	624	100	67
Nitrate of soda	936	150	46
Nitrate of soda	1,248	200	37
Sulfate of ammonia	244	50	67
Sulfate of ammonia	488	100	48
Sulfate of ammonia	732	150	12
Sulfate of ammonia	976	200	0
5–8–5 fertilizer	1,000	50	79
5–8–5 fertilizer	2,000	100	9
5–8–5 fertilizer	3,000	150	4
5–8–5 fertilizer	4,000	200	0

soda, gave better control than equivalent amounts of nitrogen used alone in any of the three forms tested.

In a field test, calcum cyanamide used at rates of 1,000 and 2,000 pounds per acre, broadcast and disced-in a week before planting, gave no control. Both treated and untreated areas showed 100 per cent infection with *Aphanomyces* and gave practically no yields. In 4 by 4-feet outdoor soil frames, on the other hand, calcium cyanamide, applied at rates of 1,000 and 1,500 pounds per acre and supplemented with superphosphate and potash in quantities equivalent to 1,000 pounds of a 0-8-5 fertilizer for two consecutive years, gave excellent control of root rot and higher yields than treatment with 1,000 or 2,000 pounds per acre of a 5-8-5 fertilizer.

It seems evident that calcium cyanamide, like nitrate of soda and sulfate of ammonia, has a certain amount of effect in delaying or preventing root infection by *Aphanomyces euteiches*, although the exact condition necessary for this action to become effective is not known.

EFFECT OF CALCIUM CYANAMIDE ON SCAB OF BEETS (ACTINOMYCES SCABIES)

A greenhouse pot-test was conducted with beets grown on a soil taken from a scabby beet-field and treated with calcium cyanamide in quantities equivalent to 100 to 400 pounds of nitrogen per acre. The higher quantities were sufficient to produce conspicuous cyanamide toxicity, but no decrease in scabbiness of the beets resulted. Abundant infection occurred in all cases.

SUMMARY AND CONCLUSIONS

Calcium cyanamide applied to the soil in quantities as large as 10,000 pounds per acre caused a marked change in the number of fungi, bacteria, and actinomyces as determined by the plating method. A greater decrease in the number of fungi resulted in soils which were near the neutral point in soil reaction than in soils which were more acid. After calcium cyanamide was applied to the soil, the number of bacteria and actinomyces decreased temporarily then increased very rapidly for about 30 days, after which they again decreased to the normal. In one case the number of bacteria in the treated soil was 92 times the number in the untreated soil.

The effect of calcium cyanamide on the soil microflora seemed to be more closely correlated with the soil reaction than with the quantity of material used.

Both calcium cyanamide and hydrated lime proved to be effective in controlling club-root of crucifers caused by *Plasmodiophora brassicae*.

Calcium cyanamide was more effective in controlling club-root in soil with a relatively high pH value. In pot cultures, 200 pounds of calcium cyanamide per acre gave a fair control of club-root on a soil with an original pH of 6.4, whereas an application of 800 pounds per acre gave only a slight decrease in clubbing in a soil with an initial reaction of pH 4.6.

In soils which were nearly neutral, calcium cyanamide alone gave satisfactory club-root control, but in a very acid soil the quantity of calcium cyanamide necessary to give control proved to be toxic to the crop immediately following.

In greenhouse tests, calcium cyanamide was about two and one-half times as effective as an equal quantity of hydrated lime in controlling club-root infection shortly after application.

On field plots heavily infested with *Plasmodiophora brassicae*, liberal application of calcium cyanamide and of hydrated lime allowed an abundant development of fibrous roots on both healthy and club-root infected plants, and consequently growth was not seriously affected by the disease. On adjacent

untreated plots, on the other hand, club-root was very severe, few or no fibrous roots developed on infected plants, and many plants died early in the season.

On field plots, a combination treatment with both calcium cyanamide and hydrated lime gave better club-root control than did calcium cyanamide alone and gave higher yields than did lime alone.

Calcium cyanamide thoroughly incorporated in the soil at rates of 1,000 to 2,000 pounds per acre (2,000,000 pounds) greatly reduced seed decay and damping-off of cucumber planted immediately after treatment. Calcium cyanamide used at the rate of 5 to 50 pounds per acre of 24-inch rows and applied in close proximity to the seed immediately before planting also gave good control of damping-off and seed decay. The margin of safety between control and seed injury was very narrow, however.

Calcium cyanamide, used at rates of 1,000 to 1,500 pounds per acre in pots and on small outside soil frames, decreased the amount of pea root rot caused by *Aphanomyces euteiches*. In a field test, on the other hand, no control was obtained from applications at rates of 1,000 and 2,000 pounds per acre.

In a pot test, calcium cyanamide gave no control of beet scab caused by *Actinomyces scabies*.

REFERENCES

(1) Allison, F. E. 1924 Effect of calcium cyanamid and related compounds on the number of microörganisms in the soil. *Jour. Agr. Res.* 28: 1159–1166.

(2) Böning, K. 1932 Das Schwarzwerden der Rettiche. *Prakt. Bl. Pflanzenbau u. Schutz* 10 (9–10): 205–219.

(3) Clark, S. W. 1934 Nematodes. *Tex. Agr. Exp. Sta. 47th Ann. Rpt. 1934:* 239.

(4) Dastur, J. F. 1931 Control of foot-rot disease of pan (Piper Betel) in the Central Provinces. *Agr. and Livestock in India* 1(1): 26–28.

(5) Doran, W. L. 1935 Diseases of herbaceous ornamental plants caused by soil-infesting fungi. *Mass. Agr. Exp. Sta. Ann. Rept.* 1934; *Bul.* 315: 26.

(6) Edwards, E. E. 1930 The control of a serious potato trouble. *Jour. Min. Agr.* [*Gt. Brit.*] 36: 234–242; (abs.) *Amer. Potato Jour.* 7(5): 149.

(7) Haenseler, C. M. 1929 Fertilizers reduce pea root rot. *N. J. Agr.* 11(3): 3.

(8) Hoerner, G. R. 1934 The use of calcium cyanamid in hop downy mildew control. Oreg. Agr. Exp. Sta. Cir. Inform. 103.

(9) Howard, L. O. 1926 The house fly and how to suppress it. U. S. Dept. Agr. Farmers Bul. 1408.

(10) Hurst, R. H., and Triffitt, M. J. 1935 Calcium cyanamid and other artificial fertilizers in the treatment of soil infested with *Heterodera schachtii*. *Jour. Helminthol.* 13(4): 201–218.

(11) Kindshoven 1928 Entseuchung des Bodens und Bekampfung der Kohlhernie mit Kalkstickstoff. *Mitt. Deut. Landw. Gesell.* 22; (Abst.) *Rev. Appl. Mycol.* 7: 691.

(12) Korff, G., and Böning, K. 1930 Beitrage zur Bodenhandlung und partiellen Bodendesinfektion. *Phytopath. Ztschr.* 2: 39–86.

(13) Kuhn, J., and Drecksel, O. 1928 Der Einfluss des Kalkstickstoff auf des Bakterienleben in Boden. *Ztschr. Pflanzenernähr. Düngung u. Bodenk.* 7: 105–118.

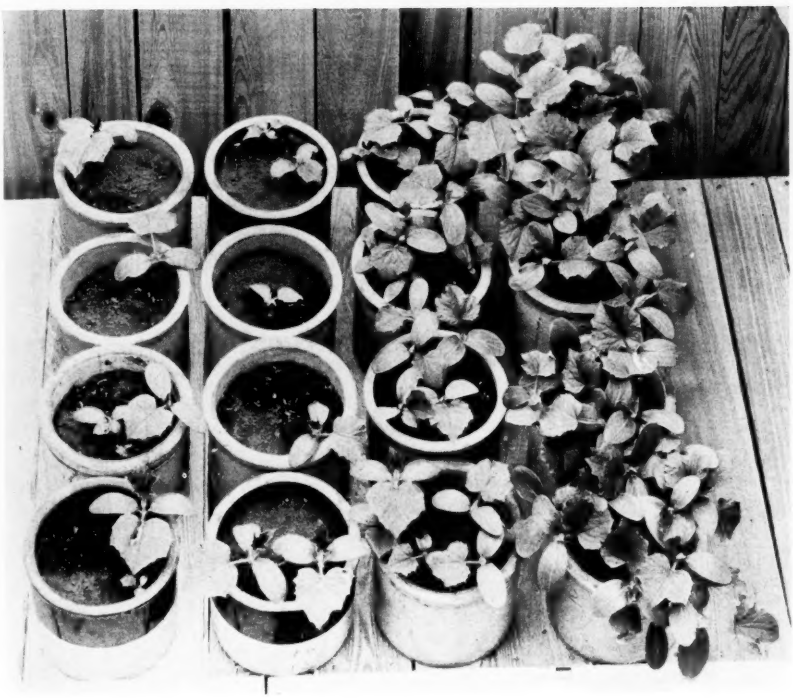
(14) Miles, M. H. 1930 Field studies on *Heterodera schachtii* Schmidt in relation to "potato sickness." *Jour. Helminthol.* 8: 103–122.

(15) MORTIMER, G. O. 1931 Getting ahead of white grubs. *Hoard's Dairyman* 76 (10).
(16) MUIR, F., AND SWEZEY, O. H. 1925 Wire worm control. *Ent. Rpt. Com. Exp. Sta., Hawaii. Sugar Planters' Assoc.* 1924–25: 12–23.
(17) PETRI, L. 1926 Toxic action of calcium cyanamid on *Blaspharaspora cambivora* and *Pythiocystis citrophthora*. *Bol. Reg. Staz. Patol. Vegetale* 6(n.s.2): 135–138.
(18) PRESTON, N. C. 1931 Prevention of finger and toe (club root) in gardens and allotments. *Jour. Min. Agr.* [*Gt. Brit.*] 38: 272–284.
(19) SHEWELL-COOPER, W. E. 1932 Club root of Brassicas. *Gard. Chron.* 91: 387–388.
(20) STEWART, G., AND BATEMAN, A. H. 1926 Field studies on sugar beet nematode. Utah Agr. Exp. Sta. Bul. 195.
(21) WALKER, J. C., AND LARSON, R. H. 1935 Calcium cyanamid in relation to control of club root of cabbage. *Jour. Agr. Res.* 51: 183–189.
(22) WATSON, J. R. 1917 Combating nematodes by the use of calcium cyanamid. *Fla. Agr. Exp. Sta. Ann. Rpt.* 1916: 55R–63R.
(23) WATSON, J. R. 1917 The control of root knot by calcium cyanamid. Fla. Agr. Exp. Sta. Bul. 136.
(24) WATSON, J. R. 1921 The control of root knot. Fla. Agr. Exp. Sta. Bul. 159.
(25) WOLFF, A., AND WOLFF, G. 1930 Ueber den Einfluss des Kalkstickstoffs auf die Mikroflora des Bödens. *Centbl. Bakt.* (II) 81: 221–230.

PLATE 1

EFFECT OF CALCIUM CYANAMIDE ON SEED DECAY AND POST-EMERGENCE DAMPING-OFF OF CUCUMBERS

Vertical rows, left to right, calcium cyanamide per acre: Row 1, none; Row 2, 400 pounds; Row 3, 800 pounds; Row 4, 1,200 pounds. Horizontal rows, top to bottom, hydrated lime per acre: Row 1, none; Row 2, 500 pounds; Row 3, 1,000 pounds; Row 4, 2,000 pounds.



THE RELATION BETWEEN THE CHEMICAL NATURE OF THE SUBSTRATE AND THE DEGREE OF CHLOROSIS IN CORN[1]

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It has been commonly observed that corn plants grown in complete nutrient media often develop chlorosis. This type of chlorotic condition in the leaves is intervenal in nature and is not associated with the total absence of any essential mineral in the nutrient medium. That is, this type is distinguishable from those types which occur under conditions of magnesium or manganese deficiency such as have been amply described by Pettinger et al. (21). Plate 1 illustrates the type of chlorosis observed in the experiments reported herein.

This chlorosis has been observed under, and ascribed to, a wide range of nutritional conditions. It has been attributed to maladjustment of the pH of the substrate, to an excessively high nitrate nitrogen content of the growing medium, to sodium toxicity, and to excess phosphate in the nutrient supply, in addition to being "lime-induced." Inasmuch as the nature of the symptoms in the plants observed under these varied conditions are very similar, it is reasonable to assume that the same mechanisms within the plant are disturbed in all these various conditions which induce the same type of chlorotic symptoms.

Pettinger et al. (21) ascribed to an excess of sodium the type of chlorosis under consideration. They observed that this type appeared in cultures that received an excess of nitrate added as sodium nitrate. They also observed it in excess phosphate cultures in which the additional phosphate was supplied as mono-basic sodium phosphate. When the practice of adding additional sodium nitrate was discontinued, the plants regained a normal green color, which led Pettinger and his associates to believe that the disorder was due to sodium toxicity.

Olsen (18) observed this type of chlorotic condition in corn plants grown in nutrient cultures supplied with an inorganic form of iron, and with the pH value of the solution adjusted in the range of from 6.0 to 7.0. He ascribed the condition to ferric phosphate precipitation within the plant, causing iron unavailability to the tissues of the plants.

In support of Olsen's contention, Mattson (17), in his cataphoretic studies on inorganic ferric compounds, found many of them to be instantly precipitable

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within the pH range of 4.0 to 7.0. Further, as shown by the work of Patten and Mains (20), the range of iron precipitation in HCl solutions extended from pH 3.5 as the lower limit to pH 6.0 as the upper limit. These ranges of iron precipitation are well within that found in the tissues of plants (25).

Loehwing (14, 15) found that the H-ion concentration of the expressed sap of wheat plants grown on limed soils is considerably lower than that of the sap of plants grown on unlimed soils and that the plants grown with high lime display chlorosis and iron immobility. Ingalls and Shive (9) observed that the soluble (filterable) iron content of plants varies directly with H-ion concentration variation brought about by changes in light intensity from day to night and that plants in which the tissue fluids have a low H-ion concentration show high total and relatively low soluble iron content, whereas those in which the tissue fluids have high hydrogen-ion concentration values show low total iron and relatively high soluble iron content. The importance of these findings was amplified by those of Oserkowsky (19) in which it was shown that the chlorophyll content of plants bears no relation to total iron content but does bear a direct relation to a small fraction of the total iron, which is proportional to the extractable iron. Rogers and Shive (22) observed by means of microchemical methods that iron accumulations usually occur in high pH tissues lying adjacent to relatively low pH tissues with a steep pH gradient between. They concluded from chemical analyses that the iron in these accumulations is in a precipitated form. No iron accumulations were found in plants with low pH tissues throughout.

These latter considerations suggest that, if the pH of the plant tissues could be modified, this might obviate any difficulty in iron availability within those tissues; but there is evidence (2, 6, 16) that the pH of a given type of cell may not be changed by a change in environmental conditions. Yet, it must be assumed that the proportions of the more acid tissues to the less acid tissues must vary considerably in order to account for the wide variation in the pH of the expressed sap of a given species.

In view of these observations, a series of widely differing nutritional substrates was devised for the purpose of studying the development of chlorosis under these varied conditions and of seeking a correlation of such observations with certain chemical properties within the plant. Specifically, corn plants were grown in (*a*) two H-ion concentration series in each of which the pH values of the nutrient solution were varied from 3.0 to 8.0: in the first series the cultures were supplied with nitrate nitrogen only and in the second series, with both nitrate and ammonium nitrogen; (*b*) a series in which the proportions of the various ionic components were varied; and (*c*) two concentration series in each of which the osmotic concentration of the growing medium was varied from 0.1 atmosphere to 3.0 atmospheres: in the first of the series the cultures were supplied with nitrate nitrogen only and in the second, with both nitrate and ammonium nitrogen. It was thought that by analyzing the expressed sap of these plants for acidity, phosphorus, and nitrate nitrogen some

insight might be gained as to why these different substrates produce similar plant responses with regard to chlorosis.

METHODS

Growing the plants

The plants were all grown from carefully selected seeds of the Dave Croshaw strain of Reed's Yellow Dent corn. Sixteen seeds were planted in each of 2-gallon percolators of washed quartz sand. When the seedlings were approximately 2 inches high, the five most uniform seedlings in each culture were selected, and the others were removed after the percolators had been flooded with tap water to facilitate the removal of the entire root system of the seedlings to be discarded. This procedure made possible the obtaining of a very uniform stand of plants. Duplicate cultures were used for each treatment.

With two exceptions, the nutrient solutions used are modifications of either the R_3S_3 solution (13) or the $T_3R_1C_3$ solution (11). The solutions $T_2R_4C_2$ and $T_1R_7C_1$, were also based upon the series of solutions devised by Jones and Shive (11). All solutions used, however, had an osmotic concentration of approximately 0.5 atmosphere except those employed in the series of cultures in which the concentration of the solution was the variable factor. The composition of the solutions used is given in tables 1, 2, 3, 4, and 5.

In addition to the salts indicated in these tables, each solution contained 2 p.p.m. of iron as ferrous sulfate and 0.5 p.p.m. each of boron and manganese added as boric acid and manganese sulfate respectively. The solution was applied at the rate of approximately 1 liter per day by the constant drip method of Shive and Stahl (24), and, in addition, each culture was flushed each morning with 1 liter of the adjusted nutrient solution, with the exception of the cultures in the pH series which were flushed with 2 liters of solution each morning in order to maintain a more constant pH level of the substrate.

Harvesting the plants and preparing tissue for analysis

The plants of the pH series were harvested on August 17, those of the variable ion proportion series on August 18, and those of the concentration series on August 19; i.e., in each case the plants were harvested 28 days after the planting date. At this time they were approximately 90–100 cm. high. They were harvested at such an early date in order to avoid maximum differentiation of tissues, which would obviously detract from the significance of the composite samples used.

Just previous to being harvested, the cultures were scored for severity of chlorosis according to the method of Free (3).

The plants were severed at the surface of the sand by means of a stainless steel knife. Those from each of the duplicate treatments were then weighed separately. Subsequent to the weighing and prior to the mincing of the tissue for aliquoting, the lower 4 inches of the stalks were severed and discarded.

This was done to avoid contamination of the sample by adsorbed nutrient salts which unavoidably come in contact with this portion of the stem during the process of regular flushing of the cultures.

After the ten plants had been minced with the stainless steel knife, the tissue was thoroughly mixed and an aliquot of 100 gm. weighed out for dry weight determination and certain analyses. From 300 to 400 gm. of tissue was immediately placed in a clean, dry, glass top fruit jar, sealed, and placed in an ice salt bath at −15°C. After being in the freezing bath for 48 hours, the tissue was thawed in water before the jar was unsealed. The juice in this tissue was then quickly expressed by means of a screw-press which employed a glass vessel to hold the tissue and exerted the pressure with a paraffined wooden plunger. This was done to preclude iron contaminations. As soon as the juice was obtained, it was filtered through a series of filter papers in a Büchner funnel by use of moderate suction. Aliquots were taken from this expressed sap for pH and titrable acidity determinations, nitrate and ammonium nitrogen, and mineral analysis.

Analyses of tissues and expressed juices

The H-ion concentration of the expressed sap was determined by means of a Leeds and Northrup Type K Potentiometer, employing a hydrogen electrode and a calomel half-cell. The same aliquot of sap was then titrated potentiometrically to pH 8.4 by means of N/10 KOH, in order to secure a value for the buffer capacity of the expressed juice.

The nitrate and ammonium nitrogen content of the expressed sap was determined by the aspiration method of Sessions and Shive (23).

The aliquot of the expressed sap used for mineral analysis was evaporated to dryness on a steam bath and the residue digested with aqua regia. The aqua regia was then evaporated off and the clear crystalline residue dissolved in N/2 HCl by warming on a steam bath. Phosphorus was determined by the method of Truog and Meyer (27).

EXPERIMENTAL OBSERVATIONS

External appearance of plants grown in pH series

Nitrogen supplied as nitrate. As indicated in table 1, the pH of the substrate in which these plants were grown was adjusted by adding phosphates of different basicity to the nutrient solution. In scoring the plants for chlorotic intensity, five arbitrary levels were chosen, varying from total absence to a severity similar to that shown in plate 1. In every case, there was a very good agreement between duplicate cultures of a treatment as to degree of chlorosis.

Excepting the variation in chlorotic intensity, there were no other marked external differences in these plants. Discounting the chlorosis, the plants possessed a general bright green color, i.e., the shade of leaf coloration which is usually associated with plants making rapid vegetative growth. It was quite apparent that the height and diameter of the stalks of the plants grown with

the pH 3.0 solution were less than the corresponding dimensions of plants of any of the other treatments. The plants grown with culture solutions of pH 8.0 were tallest but were only slightly taller than those in the other treatments.

The most striking observation with respect to this series of plants was the continual increase in severity of chlorisis with increase in pH of the substrate from 3.0 to 7.0; i.e., the plants grown in solutions of pH value 3.0 were nearly free from any evidence of chlorosis, whereas the plants grown in solutions of pH 7.0 were severely chlorotic. With a further increase in the pH of the nutrient medium to 8.0, the plants grown therein were characterized by nearly

TABLE 1

Composition of the modified R_3S_3 solutions adjusted to different pH values with nitrate as the sole source of nitrogen

pH of solution	Volume molecular concentrations						
	$Ca(NO_3)_2$	$MgSO_4$	H_3PO_4	KH_2PO_4	K_2HPO_4	K_3PO_4	KOH
2.99	.0034	.0023	.0017	.0017			
3.96	.0034	.0023	.0001	.0033			
4.95	.0034	.0023		.0031	.0003		
5.97	.0034	.0023		.0019	.0015		
7.06	.0034	.0023			.0021	.0013	
8.23	.0034	.0023				.0025	.0034

TABLE 2

Composition of the modified $T_3R_1C_3$ solutions adjusted to different pH values with both nitrate and ammonium as sources of nitrogen

pH of solution	Volume molecular concentrations							
	$Ca(NO_3)_2$	$MgSO_4$	$(NH_4)_2SO_4$	H_3PO_4	KH_2PO_4	K_2HPO_4	K_3PO_4	KOH
2.97	.0022	.0024	.0014	.00155	.0016			
4.40	.0022	.0024	.0014	.00010	.0031			
4.98	.0022	.0024	.0014		.0028	.00038		
6.02	.0022	.0024	.0014		.0015	.00168		
7.05	.0022	.0024	.0014			.00225	.00095	
8.29	.0022	.0024	.0014				.00275	.00125

complete freedom from chlorosis. This seemingly anomalous freedom from chlorisis by corn plants grown at pH 8.0 had been observed in a preliminary experiment, and Olsen (18) has made this same observation with corn plants grown with an inorganic source of iron.

Nitrogen supplied as both ammonium and nitrate. These plants, grown with nutrient solutions the compositions of which are given in table 2, were harvested the same day as those previously discussed.

Exclusive of chlorosis considerations, these plants had leaves of a very deep green luster in marked contrast to the leaves of the corresponding series not

receiving ammonium nitrogen. It is of interest to note that Jacobson and Swanback (10) observed this same coloration phenomenon incident to ammonium nutrition with tobacco plants. The pH 3.0 plants showed definite symptoms of ammonium toxicity by the wilting, withering, and drying up of the lower leaves. These plants made less growth than any in the other treatment. The pH 8.0 plants of this series displayed somewhat inferior growth also. Otherwise, the appearance of the plants in the various treatments was noticeably uniform.

The plants grown at pH values of 5.0, 6.0, and 7.0 were entirely free from chlorosis; in fact, the leaves were uniformly deep green in color. Chlorosis of the plants in the other treatments was only slight, however. It was rather significant that the pH values of the culture solutions in this series which produced plants tending to become chlorotic, namely, pH 3.0 and 8.0, were the same ones which produced plants most free from chlorosis in the pH series receiving nitrate nitrogen only. In fact, one of the outstanding observations of these experiments was the marked influence upon the plants of the presence of the ammonium ion in the nutrient solution. This suggests that the status of certain internal processes is modified by nitrogen absorption in the form of cation as well as of anion.

External appearance of plants grown in variable proportion series

These plants were grown in various ionic proportions of the nutrient media as indicated in table 3. Aside from the differences in nutritional response shown by the comparison of chlorotic intensities, there were a number of very apparent growth variations in the plants of the various treatments. The R_3S_3 cultures and the high nitrogen cultures made the best growth. The growth response was only slightly lower in the high potassium cultures, but appreciably lower in the high calcium and high magnesium cultures, than in the high nitrogen cultures. The amount of growth made by the high phosphorus cultures was considerably less than that made with the basic solution R_3S_3, whereas that of the high sulfur cultures was only slightly lower than that made with the R_3S_3 solution. It is interesting to note that the high phosphorus and high sulfur treatments showed this marked difference in growth response with the same level of the nitrate supply. Increasing the proportion of the ammonium sulfate in the substrate from one part to seven parts in a total of ten was accompanied by a very marked decrease in growth. The plants receiving the $T_1R_7C_1$ solution showed considerable ammonium toxicity.

The plants receiving the basic R_3S_3 solution were severely chlorotic. When the anions were maintained in the same proportions as in the R_3S_3 solution, variation in cation proportions produced the following results: Plants in the high potassium cultures were only slightly chlorotic, those in the high calcium cultures were moderately chlorotic, and those in the high magnesium cultures were also moderately chlorotic. When the cations were held in the same proportions as in the R_3S_3 solution and the anion proportions varied, the plants

grown in the high phosphorus and high nitrogen cultures were severely chlorotic, and those grown in the high sulfur cultures were free from chlorosis. Plants receiving one osmotic part of ammonium sulfate (out of a total of ten) in the nutrient solution were free from chlorosis, those receiving four parts were very slightly chlorotic, and those receiving seven parts were moderately chlorotic.

TABLE 3

Composition of solutions used in the variable ion proportion series

	VOLUME MOLECULAR CONCENTRATIONS									
	KH_2PO_4	$Ca(NO_3)_2$	$MgSO_4$	$(NH_4)_2SO_4$	KNO_3	K_2SO_4	$CaH_4(PO_4)_2$	$CaSO_4$	$MgH_4(PO_4)_2$	$Mg(NO_3)_2$
R_3S_3	.0034	.0034	.0023							
High K	.0034	.0012	.0011		0022	.00115				
High Ca	.0010	.0034	.0011				.0024	.00115		
High Mg	.0010	.0012	.0023						.0024	.0022
High P	.0034	.0012	.0011				.0022		.00115	
High N	.0010	.0034	.0011		.0024					.00115
High S	.0010	.0012	.0023			.0024		.0022		
$T_3R_1C_3$	.0032	.0022	.0036	.0007						
$T_2R_4C_2$	.0021	.0014	.0024	.0028						
$T_1R_7C_1$	.0011	.0007	.0012	.0049						

TABLE 4

Composition of nutrient solutions of the concentration series with nitrogen supplied solely as nitrate

OSMOTIC CONCENTRATION	VOLUME MOLECULAR CONCENTRATIONS		
	KH_2PO_4	$Ca(NO_3)_2$	$MgSO_4$
atmos.			
0.1	.00068	.00068	.00045
0.5	.00340	.00340	.00225
1.5	.01020	.01020	.00675
3.0	.02040	.02040	.01350

External appearance of plants grown in concentration series

Nitrogen supplied as nitrate. The nutritional treatment of the plants in this series was concerned with the varying of the osmotic concentration of the nutrient solution from 0.1 atmosphere to 3.0 atmospheres. The composition of these solutions is given in table 4.

Plants grown at the 0.5 atmosphere concentration made the best growth; either increasing or decreasing the total concentration from this point was accompanied by a decrease in growth. Since a relatively high concentration of the substrate tends to induce physiological drought, an explanation of the decreased growth at the higher concentrations is very apparent. The rela-relatively low growth response of the plants grown in the 0.1 atmosphere con-

centration cultures was undoubtedly due, in a large measure, to an insufficient nitrogen supply.

Plants grown at 0.1 atmosphere concentration were free from chlorosis. This symptom increased in severity with increase in osmotic concentration of the substrate, whereas the plants receiving the nutrient supply at 3.0 atmospheres concentration were severely chlorotic.

Nitrogen supplied as both nitrate and ammonium. As shown by table 5, solutions varying from 0.1 to 3.0 atmospheres concentration were supplied to these plants. As in the previous concentration series, maximum growth was made at the 0.5 atmosphere concentration. Increasing or decreasing the concentration from this level was accompanied by a decrease in growth response, nitrogen being the limiting factor at the low concentration, and physiological drought showing its usual effect on growth at the higher concentrations. As was the case in the pH series the inclusion of ammonium nitrogen in the nutrient solution was associated with the appearance of a deep green luster in the leaves of the plants so treated.

TABLE 5

Composition of nutrient solutions of the concentration series with nitrogen supplied as nitrate and ammonium

OSMOTIC CONCENTRATION	VOLUME MOLECULAR CONCENTRATIONS			
	KH_2PO_4	$Ca(NO_3)_2$	$MgSO_4$	$(NH_4)_2SO_4$
atmos.				
0.1	.00063	.00043	.00047	.00028
0.5	.00315	.00215	.00235	.00141
1.5	.00945	.00645	.00705	.00420
3.0	.01890	.01290	.01410	.00840

Plants grown at 0.1 and 0.5 atmosphere concentration were entirely free from chlorosis. When the concentration of the substrate was increased above 0.5 atmosphere, chlorosis became apparent, the symptom becoming severe in the 3.0-atmosphere concentration plants.

Expressed sap of plants grown in pH series

Nitrogen supplied as nitrate. The relationships between the degree of chlorosis of the corn plants and the acidity, phosphate, and nitrate content of the expressed sap as affected by variation in pH of the substrate, with nitrogen supplied as nitrate, are shown graphically in figure 1. The data from which these curves were constructed are presented in table 6.

The pH of the expressed sap was decidedly the lowest for the pH 3.0 plants. That of the pH 4.0 plants was appreciably higher. With further increases in pH of the growing medium up to 7.0, there was a slight but doubtfully significant increase in the pH of the expressed sap. The pH of the sap of the plants grown with the pH 8.0 solution was slightly lower than that of the

plants grown with the pH 7.0 solution. In general, these data agree with those of Loehwing (15) in implying that an increase in pH of the substrate decreases the active acidity of the expressed plant sap. It is questionable whether some of the minor variations in pH of expressed sap among the treatments were significant. Nevertheless, there is a fair agreement between the geneal trends of the sap pH and the chlorosis score curve, both reaching a maximum in the plants of the pH 7.0 cultures. Furthermore, when the heterogeneous nature of expressed plant sap is taken into account, it is apparent that its observed pH value is the composite of the pH values of all the divers tissues of the plants. Thus a very significant modification of the pH of the fluids present in the conducting system of the plant might induce only a minor deviation in the composite pH value of the expressed sap.

There does not appear to be any simple relationship between the active acidity of the sap of these plants and the total acidity. Although the expressed

TABLE 6

Degrees of chlorosis, titrable acidity, and phosphate and nitrate content of the expressed sap of corn plants as affected by variation of the pH of the substrate—nitrogen supplied as nitrate

pH OF NUTRIENT SOLUTION	DEGREE OF CHLOROSIS	AVERAGE CHLOROSIS SCORE	pH OF EXPRESSED JUICE	TITRABLE ACIDITY PER 10 ML. JUICE	P PER 10 ML. JUICE	NO_3–N PER 10 ML. JUICE	AVERAGE DRY WEIGHT TOPS PER PLANT	H_2O PER GM. DRY WEIGHT
				m.e.	*mgm.*	*mgm.*	*gm.*	*gm.*
3.0	Very slight	1	5.41	0.364	7.26	1.2	2.86	15.20
4.0	Very slight	8	5.62	0.241	5.53	2.3	3.02	17.00
5.0	Slight	16.5	5.68	0.259	5.87	2.7	2.97	17.55
6.0	Moderate	30	5.72	0.264	6.53	3.1	3.13	16.67
7.0	Severe	52.5	5.74	0.292	7.09	3.2	3.09	16.65
8.0	Very slight	3	5.69	0.219	4.71	1.3	3.44	16.65

sap of the plants grown in the pH 3.0 cultures had both the highest H-ion concentration (pH 5.41) and the highest titrable acidity (0.364 m.e. per 10 ml. sap), that from the other plants in this series showed no consistent relationship between these quantities. A secondary maximum, however, is shown in the curve of titrable acidity for the plants of the pH 7.0 cultures, for the expressed sap of which also is shown a minimum of active acidity.

A consideration of the variation in phosphorus content of the expressed sap of these plants presents an explanation for the titrable acidity variation. It is known that phosphate is a very active buffer over the pH range used in the titration procedure; it is not surprising, therefore, that such a close relationship between the phosphorus content of the juice and the titrable acidity should have been observed. Olsen (18) found the same type of variation in phosphorus content of corn plants over this pH range, with the exception of those plants of the pH 3.0 treatment which he did not include. As similarly observed by Olsen, there is an excellent correlation between the degree of chlorosis

and the phosphorus content of the corn plants over the pH range of the substrate from 4.0 to 8.0. Although plants of the pH 3.0 cultures contained the highest phosphorus content and showed the least chlorosis, it should also be recalled that they exhibited the highest value for active acidity.

Data for the nitrate nitrogen content of these plants were included because of the frequent observations that corn plants receiving a high supply of nitrate

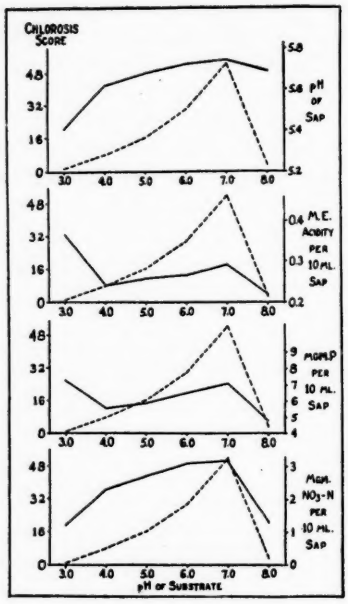


FIG. 1

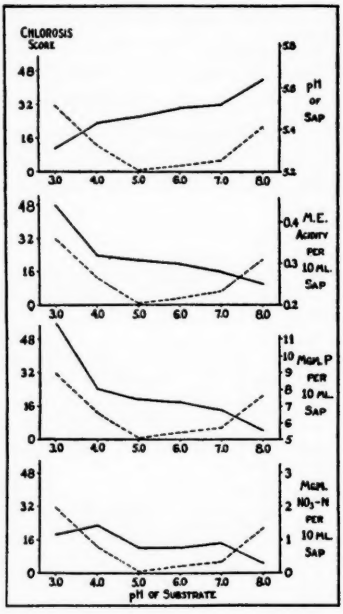


FIG. 2

FIG. 1. RELATION BETWEEN DEGREE OF CHLOROSIS, COMPONENTS OF THE EXPRESSED SAP, AND pH OF THE SUBSTRATE, NITROGEN SUPPLIED AS NITRATE

Dotted line indicates chlorosis score

FIG. 2. RELATION BETWEEN DEGREE OF CHLOROSIS, COMPONENTS OF THE EXPRESSED SAP, AND pH OF THE SUBSTRATE, NITROGEN SUPPLIED BOTH AS NITRATE AND AMMONIUM

Dotted line indicates chlorosis score

nitrogen display a marked tendency to become chlorotic. Figure 1 indicates a rather marked correlation between the nitrate content of the plants and the intensity of chlorosis.

Iron determinations were made on these plants, but, as is usually observed, there was no correlation between the total iron content of the plants and the degree of chlorosis.

Nitrogen supplied as both ammonium and nitrate. Figure 2 presents the

relationships in graphic form for this series. The graphs were constructed from the data presented in table 7. The pH of the expressed sap shows a continual increase from a value of pH 5.35 for the sap of the plants grown in the pH 3.0 solution to pH 5.64 for the sap of the plants grown in the pH 8.0 solution. These values are all appreciably lower than the corresponding ones for the plants of the nitrate nitrogen series. This observation that a supply of ammonium nitrogen tends to lower pH of the expressed sap has been noted many times. As shown in figure 2, the increase in pH of the expressed sap with increase in pH of the substrate was rather small, with the exception of the jump in pH value of the sap from the plants of the pH 7.0 to that of the pH 8.0 cultures. It should be noted that for the higher pH range of the nutrient medium there was a very close relationship between the degree of chlorosis and the pH of the expressed sap but that this relationship does not hold at the lower pH range of the substrate.

TABLE 7

Degrees of chlorosis, titrable acidity, and phosphate and nitrate content of the expressed sap of corn plants as affected by variation of the pH of the substrate—nitrogen supplied as both nitrate and ammonium

pH OF NUTRIENT SOLUTION	DEGREE OF CHLOROSIS	AVERAGE CHLOROSIS SCORE	pH OF EXPRESSED JUICE	TITRABLE ACIDITY PER 10 ML. JUICE	P PER 10 ML. JUICE	NO_3–N PER 10 ML. JUICE	AVERAGE DRY WEIGHT TOPS PER PLANT	H_2O PER GM. DRY WEIGHT
				m.e.	*mgm.*	*mgm.*	*gm.*	*gm.*
3.0	Slight	31.5	5.31	.441	11.90	1.16	2.11	13.25
4.0	Very slight	13	5.43	.318	8.06	1.42	2.65	16.61
5.0	Free	0.5	5.46	.306	7.41	0.77	2.79	16.50
6.0	Free	3	5.50	.297	7.25	0.78	2.89	15.85
7.0	Free	6.5	5.52	.278	6.72	0.91	3.10	15.92
8.0	Slight	21.5	5.64	.250	5.58	0.32	2.64	15.05

The titrable acidity of these plants shows a general downward trend with increasing pH of the growth medium, with the most marked decrease occurring between the plants of the pH 3.0 and those of the pH 4.0 cultures. This quantity shows some relationship with the chlorotic tendency of the plants in the lower pH range of the substrate but not in the upper range.

As in the previously discussed series the titrable acidity curve follows the trend of the curve of the phosphorus content of the expressed sap. On the whole, the phosphorus content of the sap of the plants receiving ammonium nitrogen was significantly higher than that of plants receiving only nitrate nitrogen. Correspondingly, the titrable acidity was, for the most part, higher in the plants receiving ammonium nitrogen than in those receiving nitrate nitrogen only.

It is apparent that the phosphorus content of the plants of the pH 3.0 cultures (fig. 2) was extremely high and that, although the pH of the expressed sap of these plants was the lowest of any in the series, the plants showed the

highest score for chlorisis. In contradistinction, however, the plants of the pH 8.0 cultures with the lowest phosphorus content also displayed a slight tendency to become chlorotic, but these plants had the highest pH of the expressed sap. It appears, therefore, that it is not quite justifiable to attempt to associate chlorotic tendency entirely with either pH of the sap or phosphorus content separately.

As to the nitrate nitrogen content of the expressed sap of the plants of this series in relation to chlorosis, the main point to be brought out is that the nitrate nitrogen content was, on the whole, relatively low, whereas these plants, in general, displayed remarkable freedom from chlorosis. This fact was previously observed by Jones and Shive (12), who showed that the presence of ammonium in the nutrient solution aided the plant in its utilization of iron, as indicated by freedom from chlorosis. There was not, however, a perfect agreement between the trends of the curve showing chlorotic tendency and nitrate nitrogen content.

In a comparison of the response of the corn plants in this pH series with the previous one, in which the ammonium ion was not supplied, certain marked differences merit interpretation. Although there was considerably more evidence of chlorosis, on the average, in the plants grown with the solutions containing nitrate only than in those grown with the solutions containing both nitrate and ammonium nitrogen, it was rather striking that the two pH levels (3.0 and 8.0) in the latter series which produced plants with appreciable evidence of chlorisis were the same pH levels in the nitrate series which permitted plants to develop with the least symptoms of chlorosis. It should be recalled that the trends of both the pH and the phosphorus curves are distinct in the two series. In discussing the chlorosis of specific cultures of these two series, it has been possible to point out the covariance of the chlorotic intensity with either sap acidity or phosphate content. An interrelationship between these two components in their effect on the degree of chlorosis of the plant is here suggested.

Expressed sap of plants grown in variable ion proportion series

As indicated in figure 3 and in table 8, the plants grown with solution R_3S_3 (table 3) showed the highest pH of the expressed sap and a higher degree of chlorosis than any in this series, whereas the plants grown with the solution high in nitrogen were only slightly less chlorotic and showed a slightly lower pH of the expressed sap than did the plants grown with solution R_3S_3. Yet, the two treatments producing plants practically free from chlorosis, namely, $T_3R_1C_3$ and the solution high in sulfate, did not, by any means, show the lowest pH values of the expressed sap of any plants in the series. Further, although the plants grown with solutions high in potassium and high in phosphate contained sap of nearly the same pH, the latter were severely chlorotic and the former only slightly so. The observation that the chlorotic condition of the plants increased when the osmotic parts of ammonium sulfate

in the nutrient solution were increased from one to seven, in a total of ten, could not be associated with any specific trend in the pH of the expressed sap. In this series, then, it may not be said that an exact correlation existed between the pH of the expressed juice and the availability of iron as measured by freedom from chlorosis.

The titrable acidity was highest in the severely chlorotic plants, grown with the solution high in phosphate, but was very low in the plants of two other

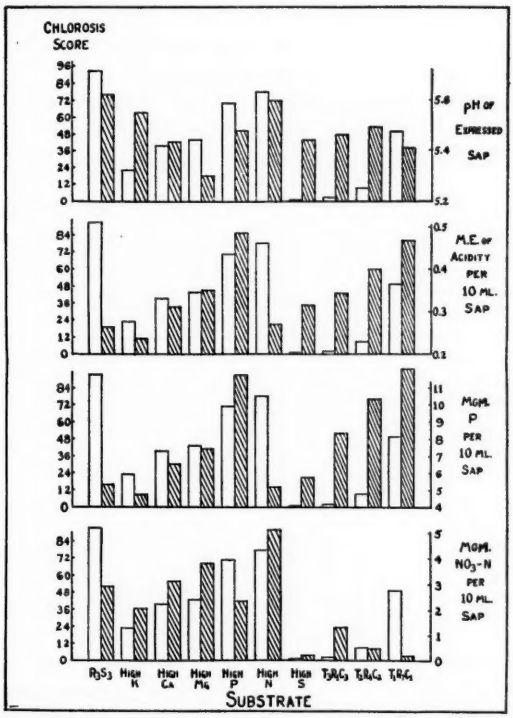


FIG. 3. RELATION BETWEEN DEGREE OF CHLOROSIS INDICATED BY THE COMPONENTS OF THE EXPRESSED SAP AND THE ION PROPORTION OF THE SUBSTRATE

Blank bars indicate chlorosis scores

treatments which produced very chlorotic plants. The titrable acidity was nearly identical for the expressed juices of the plants grown with high calcium and high sulfate, and yet the latter were entirely free from chlorosis, whereas the former were moderately chlorotic. Increasing the concentration of ammonium in the nutrient solution from one osmotic part to seven was accompanied by a significant increase in the titrable acidity of the expressed sap.

This increase in titrable acidity was accompanied also by a tendency of the plants to become chlorotic. On the whole, there does not appear to be a direct relationship between the buffer capacity of the expressed sap and the degree of chlorosis of the plants.

Because of the intimate relation between the phosphorus content of the plant sap and the values obtained for titrable acidity, the correlation between titrable acidity and chlorosis also holds for phosphorus content of the expressed sap and chlorosis.

All treatments in this series other than high sulfate, or those in which ammonium nitrogen occurred, produced plants containing considerable nitrate nitrogen in the expressed sap. Some chlorosis was evident in all of these plants. A fairly good correlation exists between the amount of nitrate in the plant sap and the intensity of the chlorotic symptoms of the plant. The plants

TABLE 8

Degrees of chlorosis, titrable acidity, and phosphorus and nitrate content of the expressed sap of corn plants grown with solutions of various ion proportions

TREATMENT	DEGREE OF CHLOROSIS	CHLOROSIS SCORE	pH OF EXPRESSED JUICE	TITRABLE ACIDITY PER 10 ML. JUICE	P PER 10 ML. JUICE	NO_3–N PER 10 ML. JUICE	AVERAGE DRY WEIGHT PER PLANT	H_2O PER GM. DRY WEIGHT
				m.e.	*mgm.*	*mgm.*	*gm.*	*gm.*
R_3S_3	Severe	92.5	5.62	.262	5.32	2.90	3.05	13.75
High K	Slight	22.5	5.55	.235	4.67	2.05	2.91	14.50
High Ca	Moderate	39.5	5.43	.309	6.49	3.10	2.49	13.78
High Mg	Moderate	44.0	5.34	.351	7.41	3.80	2.35	13.55
High P	Severe	70.5	5.48	.484	11.91	2.35	2.12	14.10
High N	Severe	77.5	5.60	.268	5.20	5.10	3.03	14.85
High S	Free	0.5	5.44	.315	5.75	.20	2.92	12.82
$T_3R_1C_3$	Free	2.5	5.46	.344	8.37	1.30	3.39	14.00
$T_2R_4C_2$	Very slight	9.0	5.49	.399	10.31	.45	2.34	14.10
$T_1R_7C_1$	Moderate	50.0	5.41	.466	12.30	.20	0.95	13.69

grown in the high sulfur cultures contained very little nitrate and were entirely free from chlorosis. One very interesting point to be emphasized is the fact that the plants grown in the high phosphate and high sulfate cultures received the same amount of nitrogen and that, although the latter plants contained very little nitrate in the sap, the plants grown in the high phosphorus solution contained a relatively high proportion of nitrate and were severely chlorotic. Although the nitrate nitrogen content of all of the ammonium plants grown with both nitrate and ammonium nitrogen was relatively low, there was the suggestion of an inverse relation between nitrate content and chlorotic tendency in the presence of this cation.

As mentioned previously, no exact correlation exists between chlorotic tendency of the corn plants and the relative values of any one of the components studied. It does appear, however, that chlorotic tendencies which

are not correlative with one component may be correlative with another. Specifically, the degree of chlorosis in the plants grown with the solution containing ammonium could not be correlated with the pH of the sap or nitrate content, but it was very closely correlated with the phosphorus content of the sap and, likewise, with titrable acidity.

Expressed sap of plants grown in concentration series

Nitrogen supplied as nitrate. As shown in figure 4 and in table 9, with increasing concentration of the substrate from 0.1 to 1.5 atmospheres a corresponding increase occurred in the pH value of the expressed juice from 5.36 to 5.58, and the degree of chlorosis correspondingly increased. The plants grown with the solution of 3.0 atmospheres concentration, however, had an intermediate pH value (5.47) of the expressed sap and were severely chlorotic.

As the osmotic concentration of the substrate was increased, there was a marked tendency for the titrable acidity of the expressed sap to decrease,

TABLE 9

Degrees of chlorosis, titrable acidity, and phosphorus and nitrate content of the expressed sap of corn plants grown with solutions of different osmotic concentrations, nitrate constituting the sole source of nitrogen

OSMOTIC CONCENTRATION	DEGREE OF CHLOROSIS	CHLOROSIS SCORE	pH OF EXPRESSED JUICE	TITRABLE ACIDITY PER 10 ML. EXPRESSED JUICE	P PER 10 ML. JUICE	NO_3—N PER 10 ML. JUICE	AVERAGE DRY WEIGHT PER PLANT	H_2O PER GM. DRY WEIGHT
atmos.				*m.e.*	*mgm.*	*mgm.*	*gm.*	*gm.*
0.1	Free	1	5.36	.365	6.05	0.40	2.97	11.06
0.5	Slight	7.5	5.49	.329	8.24	2.80	3.99	14.33
1.5	Moderate	22	5.58	.260	5.65	3.90	3.32	13.84
3.0	Severe	32.5	5.47	.263	4.25	4.45	2.95	11.95

which was just the inverse of the variation of chlorotic intensity. The phosphorus content of the expressed sap showed a maximum for the plants grown in the solution of 0.5 atmosphere concentration. Thus, there was little agreement between the phosphorus content and the chlorotic intensity curves. In this series, there was not the same relationship exhibited between phosphorus content and the titrable acidity as heretofore brought out. Evidently, the nature of the substrate was conducive to the accumulation of buffering substances, other than phosphate, in the plants grown with solutions of 0.1 and 3.0 atmospheres osmotic concentration.

There was very good agreement between nitrate accumulation in these plants and the intensity of chlorosis. Thus, from a consideration of this portion of the data alone, it might be concluded that chlorotic intensity is correlative with nitrate accumulation within the plant and, to a certain extent, also with the pH of the expressed sap. With the exception of the plants grown with solutions of the lowest concentration, an inverse relationship is

and the phosphorus content of the corn plants over the pH range of the substrate from 4.0 to 8.0. Although plants of the pH 3.0 cultures contained the highest phosphorus content and showed the least chlorosis, it should also be recalled that they exhibited the highest value for active acidity.

Data for the nitrate nitrogen content of these plants were included because of the frequent observations that corn plants receiving a high supply of nitrate

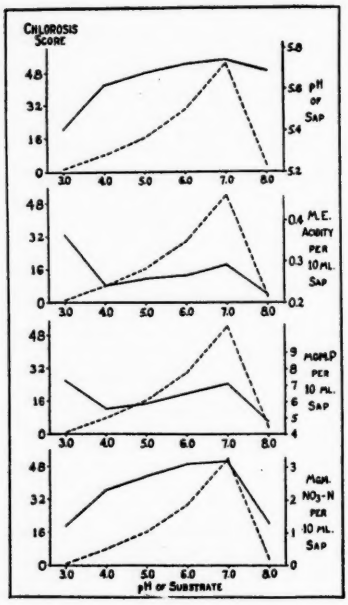


FIG. 1

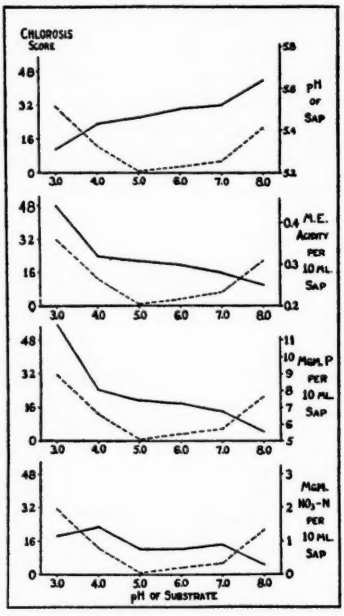


FIG. 2

FIG. 1. RELATION BETWEEN DEGREE OF CHLOROSIS, COMPONENTS OF THE EXPRESSED SAP, AND pH OF THE SUBSTRATE, NITROGEN SUPPLIED AS NITRATE

Dotted line indicates chlorosis score

FIG. 2. RELATION BETWEEN DEGREE OF CHLOROSIS, COMPONENTS OF THE EXPRESSED SAP, AND pH OF THE SUBSTRATE, NITROGEN SUPPLIED BOTH AS NITRATE AND AMMONIUM

Dotted line indicates chlorosis score

nitrogen display a marked tendency to become chlorotic. Figure 1 indicates a rather marked correlation between the nitrate content of the plants and the intensity of chlorosis.

Iron determinations were made on these plants, but, as is usually observed, there was no correlation between the total iron content of the plants and the degree of chlorosis.

Nitrogen supplied as both ammonium and nitrate. Figure 2 presents the

relationships in graphic form for this series. The graphs were constructed from the data presented in table 7. The pH of the expressed sap shows a continual increase from a value of pH 5.35 for the sap of the plants grown in the pH 3.0 solution to pH 5.64 for the sap of the plants grown in the pH 8.0 solution. These values are all appreciably lower than the corresponding ones for the plants of the nitrate nitrogen series. This observation that a supply of ammonium nitrogen tends to lower pH of the expressed sap has been noted many times. As shown in figure 2, the increase in pH of the expressed sap with increase in pH of the substrate was rather small, with the exception of the jump in pH value of the sap from the plants of the pH 7.0 to that of the pH 8.0 cultures. It should be noted that for the higher pH range of the nutrient medium there was a very close relationship between the degree of chlorosis and the pH of the expressed sap but that this relationship does not hold at the lower pH range of the substrate.

TABLE 7

Degrees of chlorosis, titrable acidity, and phosphate and nitrate content of the expressed sap of corn plants as affected by variation of the pH of the substrate—nitrogen supplied as both nitrate and ammonium

pH OF NUTRIENT SOLUTION	DEGREE OF CHLOROSIS	AVERAGE CHLOROSIS SCORE	pH OF EXPRESSED JUICE	TITRABLE ACIDITY PER 10 ML. JUICE	P PER 10 ML. JUICE	NO_3–N PER 10 ML. JUICE	AVERAGE DRY WEIGHT TOPS PER PLANT	H_2O PER GM. DRY WEIGHT
				m.e.	*mgm.*	*mgm.*	*gm.*	*gm.*
3.0	Slight	31.5	5.31	.441	11.90	1.16	2.11	13.25
4.0	Very slight	13	5.43	.318	8.06	1.42	2.65	16.61
5.0	Free	0.5	5.46	.306	7.41	0.77	2.79	16.50
6.0	Free	3	5.50	.297	7.25	0.78	2.89	15.85
7.0	Free	6.5	5.52	.278	6.72	0.91	3.10	15.92
8.0	Slight	21.5	5.64	.250	5.58	0.32	2.64	15.05

The titrable acidity of these plants shows a general downward trend with increasing pH of the growth medium, with the most marked decrease occurring between the plants of the pH 3.0 and those of the pH 4.0 cultures. This quantity shows some relationship with the chlorotic tendency of the plants in the lower pH range of the substrate but not in the upper range.

As in the previously discussed series the titrable acidity curve follows the trend of the curve of the phosphorus content of the expressed sap. On the whole, the phosphorus content of the sap of the plants receiving ammonium nitrogen was significantly higher than that of plants receiving only nitrate nitrogen. Correspondingly, the titrable acidity was, for the most part, higher in the plants receiving ammonium nitrogen than in those receiving nitrate nitrogen only.

It is apparent that the phosphorus content of the plants of the pH 3.0 cultures (fig. 2) was extremely high and that, although the pH of the expressed sap of these plants was the lowest of any in the series, the plants showed the

highest score for chlorisis. In contradistinction, however, the plants of the pH 8.0 cultures with the lowest phosphorus content also displayed a slight tendency to become chlorotic, but these plants had the highest pH of the expressed sap. It appears, therefore, that it is not quite justifiable to attempt to associate chlorotic tendency entirely with either pH of the sap or phosphorus content separately.

As to the nitrate nitrogen content of the expressed sap of the plants of this series in relation to chlorosis, the main point to be brought out is that the nitrate nitrogen content was, on the whole, relatively low, whereas these plants, in general, displayed remarkable freedom from chlorosis. This fact was previously observed by Jones and Shive (12), who showed that the presence of ammonium in the nutrient solution aided the plant in its utilization of iron, as indicated by freedom from chlorosis. There was not, however, a perfect agreement between the trends of the curve showing chlorotic tendency and nitrate nitrogen content.

In a comparison of the response of the corn plants in this pH series with the previous one, in which the ammonium ion was not supplied, certain marked differences merit interpretation. Although there was considerably more evidence of chlorosis, on the average, in the plants grown with the solutions containing nitrate only than in those grown with the solutions containing both nitrate and ammonium nitrogen, it was rather striking that the two pH levels (3.0 and 8.0) in the latter series which produced plants with appreciable evidence of chlorisis were the same pH levels in the nitrate series which permitted plants to develop with the least symptoms of chlorosis. It should be recalled that the trends of both the pH and the phosphorus curves are distinct in the two series. In discussing the chlorosis of specific cultures of these two series, it has been possible to point out the covariance of the chlorotic intensity with either sap acidity or phosphate content. An interrelationship between these two components in their effect on the degree of chlorosis of the plant is here suggested.

Expressed sap of plants grown in variable ion proportion series

As indicated in figure 3 and in table 8, the plants grown with solution R_3S_3 (table 3) showed the highest pH of the expressed sap and a higher degree of chlorosis than any in this series, whereas the plants grown with the solution high in nitrogen were only slightly less chlorotic and showed a slightly lower pH of the expressed sap than did the plants grown with solution R_3S_3. Yet, the two treatments producing plants practically free from chlorosis, namely, $T_3R_1C_3$ and the solution high in sulfate, did not, by any means, show the lowest pH values of the expressed sap of any plants in the series. Further, although the plants grown with solutions high in potassium and high in phosphate contained sap of nearly the same pH, the latter were severely chlorotic and the former only slightly so. The observation that the chlorotic condition of the plants increased when the osmotic parts of ammonium sulfate

in the nutrient solution were increased from one to seven, in a total of ten, could not be associated with any specific trend in the pH of the expressed sap. In this series, then, it may not be said that an exact correlation existed between the pH of the expressed juice and the availability of iron as measured by freedom from chlorosis.

The titrable acidity was highest in the severely chlorotic plants, grown with the solution high in phosphate, but was very low in the plants of two other

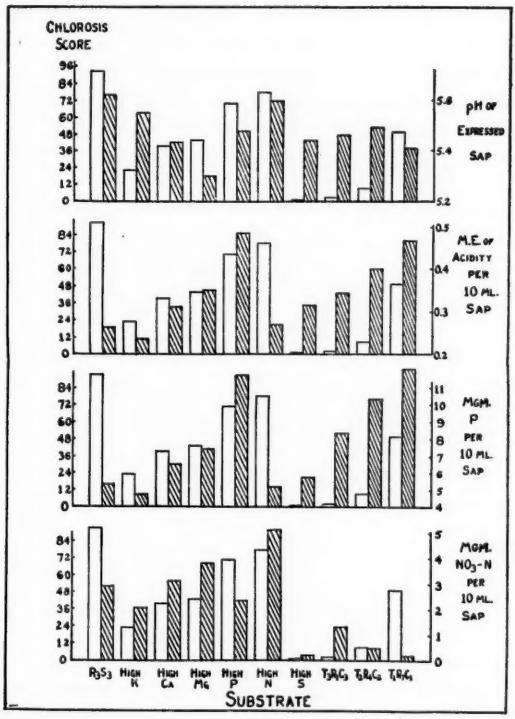


FIG. 3. RELATION BETWEEN DEGREE OF CHLOROSIS INDICATED BY THE COMPONENTS OF THE EXPRESSED SAP AND THE ION PROPORTION OF THE SUBSTRATE

Blank bars indicate chlorosis scores

treatments which produced very chlorotic plants. The titrable acidity was nearly identical for the expressed juices of the plants grown with high calcium and high sulfate, and yet the latter were entirely free from chlorosis, whereas the former were moderately chlorotic. Increasing the concentration of ammonium in the nutrient solution from one osmotic part to seven was accompanied by a significant increase in the titrable acidity of the expressed sap.

This increase in titrable acidity was accompanied also by a tendency of the plants to become chlorotic. On the whole, there does not appear to be a direct relationship between the buffer capacity of the expressed sap and the degree of chlorosis of the plants.

Because of the intimate relation between the phosphorus content of the plant sap and the values obtained for titrable acidity, the correlation between titrable acidity and chlorosis also holds for phosphorus content of the expressed sap and chlorosis.

All treatments in this series other than high sulfate, or those in which ammonium nitrogen occurred, produced plants containing considerable nitrate nitrogen in the expressed sap. Some chlorosis was evident in all of these plants. A fairly good correlation exists between the amount of nitrate in the plant sap and the intensity of the chlorotic symptoms of the plant. The plants

TABLE 8

Degrees of chlorosis, titrable acidity, and phosphorus and nitrate content of the expressed sap of corn plants grown with solutions of various ion proportions

TREATMENT	DEGREE OF CHLOROSIS	CHLOROSIS SCORE	pH OF EXPRESSED JUICE	TITRABLE ACIDITY PER 10 ML. JUICE	P PER 10 ML. JUICE	NO_3–N PER 10 ML. JUICE	AVERAGE DRY WEIGHT PER PLANT	H_2O PER GM. DRY WEIGHT
				m.e.	*mgm.*	*mgm.*	*gm.*	*gm.*
R_3S_3	Severe	92.5	5.62	.262	5.32	2.90	3.05	13.75
High K	Slight	22.5	5.55	.235	4.67	2.05	2.91	14.50
High Ca	Moderate	39.5	5.43	.309	6.49	3.10	2.49	13.78
High Mg	Moderate	44.0	5.34	.351	7.41	3.80	2.35	13.55
High P	Severe	70.5	5.48	.484	11.91	2.35	2.12	14.10
High N	Severe	77.5	5.60	.268	5.20	5.10	3.03	14.85
High S	Free	0.5	5.44	.315	5.75	.20	2.92	12.82
$T_1R_1C_3$	Free	2.5	5.46	.344	8.37	1.30	3.39	14.00
$T_2R_4C_2$	Very slight	9.0	5.49	.399	10.31	.45	2.34	14.10
$T_1R_7C_1$	Moderate	50.0	5.41	.466	12.30	.20	0.95	13.69

grown in the high sulfur cultures contained very little nitrate and were entirely free from chlorosis. One very interesting point to be emphasized is the fact that the plants grown in the high phosphate and high sulfate cultures received the same amount of nitrogen and that, although the latter plants contained very little nitrate in the sap, the plants grown in the high phosphorus solution contained a relatively high proportion of nitrate and were severely chlorotic. Although the nitrate nitrogen content of all of the ammonium plants grown with both nitrate and ammonium nitrogen was relatively low, there was the suggestion of an inverse relation between nitrate content and chlorotic tendency in the presence of this cation.

As mentioned previously, no exact correlation exists between chlorotic tendency of the corn plants and the relative values of any one of the components studied. It does appear, however, that chlorotic tendencies which

are not correlative with one component may be correlative with another. Specifically, the degree of chlorosis in the plants grown with the solution containing ammonium could not be correlated with the pH of the sap or nitrate content, but it was very closely correlated with the phosphorus content of the sap and, likewise, with titrable acidity.

Expressed sap of plants grown in concentration series

Nitrogen supplied as nitrate. As shown in figure 4 and in table 9, with increasing concentration of the substrate from 0.1 to 1.5 atmospheres a corresponding increase occurred in the pH value of the expressed juice from 5.36 to 5.58, and the degree of chlorosis correspondingly increased. The plants grown with the solution of 3.0 atmospheres concentration, however, had an intermediate pH value (5.47) of the expressed sap and were severely chlorotic.

As the osmotic concentration of the substrate was increased, there was a marked tendency for the titrable acidity of the expressed sap to decrease,

TABLE 9

Degrees of chlorosis, titrable acidity, and phosphorus and nitrate content of the expressed sap of corn plants grown with solutions of different osmotic concentrations, nitrate constituting the sole source of nitrogen

OSMOTIC CONCENTRATION	DEGREE OF CHLOROSIS	CHLOROSIS SCORE	pH OF EXPRESSED JUICE	TITRABLE ACIDITY PER 10 ML. EXPRESSED JUICE	P PER 10 ML. JUICE	NO_3–N PER 10 ML. JUICE	AVERAGE DRY WEIGHT PER PLANT	H_2O PER GM. DRY WEIGHT
atmos.				*m.e.*	*mgm.*	*mgm.*	*gm.*	*gm.*
0.1	Free	1	5.36	.365	6.05	0.40	2.97	11.06
0.5	Slight	7.5	5.49	.329	8.24	2.80	3.99	14.33
1.5	Moderate	22	5.58	.260	5.65	3.90	3.32	13.84
3.0	Severe	32.5	5.47	.263	4.25	4.45	2.95	11.95

which was just the inverse of the variation of chlorotic intensity. The phosphorus content of the expressed sap showed a maximum for the plants grown in the solution of 0.5 atmosphere concentration. Thus, there was little agreement between the phosphorus content and the chlorotic intensity curves. In this series, there was not the same relationship exhibited between phosphorus content and the titrable acidity as heretofore brought out. Evidently, the nature of the substrate was conducive to the accumulation of buffering substances, other than phosphate, in the plants grown with solutions of 0.1 and 3.0 atmospheres osmotic concentration.

There was very good agreement between nitrate accumulation in these plants and the intensity of chlorosis. Thus, from a consideration of this portion of the data alone, it might be concluded that chlorotic intensity is correlative with nitrate accumulation within the plant and, to a certain extent, also with the pH of the expressed sap. With the exception of the plants grown with solutions of the lowest concentration, an inverse relationship is

indicated between phosphorus content of the expressed sap and degree of chlorosis.

Nitrogen supplied as both nitrate and ammonium. As is indicated by the graphs of figure 5 and by table 10, no close correlation was shown between chlorotic intensity and the pH of the expressed sap of the plants of this series grown with both nitrate and ammonium nitrogen, although the plants of the

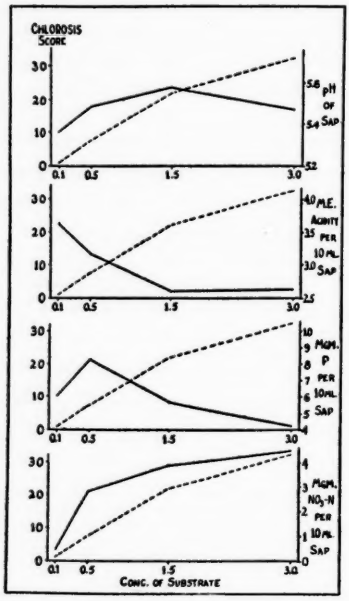


Fig. 4

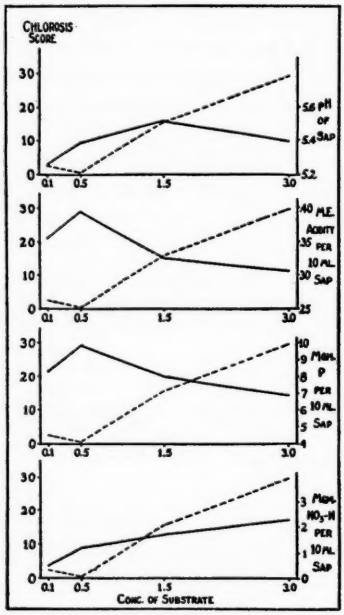


Fig. 5

Fig. 4. Relation between Degree of Chlorosis, Components of the Expressed Sap, and Concentration of the Substrate, Nitrogen Supplied Only as Nitrate

Dotted line represents degrees of chlorosis

Fig. 5. Relation between Degree of Chlorosis, Components of the Expressed Sap, and Concentration of the Substrate, Nitrogen Supplied as Both Nitrate and Ammonium

Dotted line represents degree of chlorosis

two lower concentrations that were free of chlorosis had a lower pH of the expressed sap than the plants of the two higher concentrations that were chlorotic.

It appears from the data that the chlorotic intensity of the plants in this concentration series varied inversely with phosphorus content and also with titrable acidity of the expressed sap. There is, however, direct relationship

between nitrate nitrogen content of the expressed sap and chlorotic intensity of the plants in this series. Although the marked increase of nitrate nitrogen in the sap of the plants grown with the solution of 0.5 atmosphere concentration over that of the plants grown with the solution of 0.1 atmosphere concentration was not accompanied by the appearance of any chlorotic symptoms, the plants grown at higher concentrations and containing increasing amounts of nitrate nitrogen in the sap did show chlorosis. As a whole, this series of plants, which received ammonium nitrogen, showed chlorosis in considerably lower intensity than did the plants of the concentration series which received only nitrate nitrogen.

MICROCHEMICAL OBSERVATIONS

Microchemical tests on the tissues of chlorotic plants with the potassium ferricyanide reagent showed the presence of considerable iron in the fibrovascular tissues. The blue color, however, would not appear as a result merely of applying the reagent to the sections of the tissues in question. Instead, it was necessary to treat the sections first with a 2 per cent solution of hydrochloric acid then with the potassium ferricyanide and wait several hours for the blue color to develop. This indicates that the major part of the iron in these corn plants was in the precipitated form. In fact, Gile and Carrero (4), Hoffer and Carr (7), and others have arrived at the same conclusion that the type of chlorosis discussed herein is due to iron immobility within the plant. Hoffer and Carr (7) also noted the condition to be of noticeable severity on soils high in phosphate.

TABLE 10

Degrees of chlorosis, titrable acidity, and phosphorus and nitrate content of the expressed sap of corn plants grown with solutions of different osmotic concentrations, nitrate and ammonium constituting the sources of nitrogen

OSMOTIC CONCENTRATION	INTENSITY OF CHLOROSIS	CHLOROSIS SCORE	pH OF EXPRESSED JUICE	TITRABLE ACIDITY PER 10 ML. JUICE	P PER 10 ML. JUICE	NO_3–N PER 10 ML. JUICE	AVERAGE DRY WEIGHT PER PLANT	H_2O PER GM. DRY WEIGHT
atmos.				*m.e.*	*mgm.*	*mgm.*	*gm.*	*gm.*
0.1	Free	2.5	5.26	.356	8.33	0.55	2.37	11.83
0.5	Free	0.5	5.38	.391	9.82	1.20	4.02	14.13
1.5	Slight	16.0	5.52	.327	7.96	1.70	3.89	12.14
3.0	Severe	29.5	5.39	.306	6.89	2.25	2.36	11.28

DISCUSSION

With the acceptance of the theory that the type of chlorosis herein reported is induced by iron immobility, and in view of the numerous observations which appear paradoxical in the data presented, it becomes important to emphasize the possibility of an equilibrium condition between iron solubility, pH of the

tissue fluids, and the phosphate concentration of the plant sap. For example, a relatively high pH of the tissue fluids apparently tends to precipitate iron regardless of phosphate concentration, and, by mass action, a relatively high concentration of phosphate ions tends to precipitate iron even though the acidity of the medium is rather conducive to iron solubility in the absence of high phosphate ion concentration. The interrelationship, then, between chlorosis of the plant, phosphate concentration of the sap, and pH of the tissue fluids, here pointed out, appears quite logical from the chemical standpoint.

One of the most prominent relationships observed in this study, however, was that a high nitrate content of the expressed sap of the plants was, with few exceptions, closely associated with severe chlorosis, and a low nitrate content, with relative freedom from chlorosis. It is rather to be doubted that the nitrate ion could have any direct effect on iron solubility, even though such a relationship appears to be indicated. Yet, an abundant nitrate nitrogen supply is usually associated with high vegetative vigor; that is, under such conditions a relatively high rate of metabolic activity takes place in the meristematic tissues. This type of tissue is usually observed to possess a relatively lower acidity value than other tissues in the plant (25). As stated previously, it is possible actually to observe, microchemically, iron accumulations in the more alkaline tissues. Furthermore, Hurd (8) has observed a direct relationship between the vegetative vigor of the corn plant and the pH of the expressed sap. It appears, therefore, that the relationship observed here between the nitrate content of the plant and the degree of chlorosis is explainable on the basis of the nitrogen supply's exerting a regulatory effect upon the metabolic activity.

It was quite apparent both from observation and from the data here presented that the presence of the ammonium ion in the nutrient solution was associated with a much lower degree of chlorotic intensity than when nitrate constituted the sole source of nitrogen. It was also pointed out that plants receiving ammonium nitrogen had a comparatively lower pH value of the expressed sap than those receiving nitrate nitrogen only. In this connection, it is of interest to refer to the work of Conrad (1) concerning the acidity and alkalinity changes accompanying nitrogenous changes in the soil. To quote:

> Relying upon the law of conservation of matter and from simple reactions in the main, it is shown that transformations from one form of nitrogen to another within the group N_2, urea, NH_4NO_3, NH_4NO_2, and proteins cause very little or no change in titrable acidity or alkalinity. Transformations from any one or all of this group to ammonia cause the appearance of about one equivalent of titrable alkalinity for each gram-atom of nitrogen changed. Transformations from this same group to nitric acid or nitrates result in the production of about one equivalent of titrable acidity for each gram-atom of nitrogen changed.

In plants, the reverse transformations normally take place, that is, conversion of the absorbed nitrate or ammonium to protein. It follows that the acidity and alkalinity changes would be the converse of the above; that is, nitrate assimilation would cause the appearance of alkalinity, whereas am-

monium assimilation would cause the appearance of acidity. The experimental data here presented confirm this postulate. It is quite reasonable, therefore, to interpret the lowered chlorotic intensity of corn accompanying the addition of ammonium to the nutrient medium as being the result of a higher composite acidity of the plant tissues, making for high iron solubility and availability.

It was observed by means of pH measurements of the "drip" from the bottom of the percolators used as culture vessels that plants receiving nitrogen as nitrate only, tended to change the pH of the solution from pH 4.8 to about pH 6.5, whereas those receiving both nitrate and ammonium tended to change the pH of the solution from pH 4.8 to about pH 4.0. Tiedjens and Robbins (26) made this same observation. It is reasonable to assume, therefore, that the pH of the solution films adjacent to the absorbing portions of the roots was approximately 6.5 in the case of the plants receiving nitrate only and approximately 4.0 in the case of plants receiving both nitrate and ammonium nitrogen. This lowering of the pH of the absorbing film would be instrumental in lowering the absorption rate of bases (5), and, of course, it is known that the addition of the ammonium ion to the nutrient solution decreases the absorption of other basic ions (10). It is, therefore, logical to assume that the summation of such ion activity tends to lower the pH of the plant sap as indicated by measurements made upon the composite tissue samples employed in this study.

SUMMARY

Five different series of corn plants grown in sand culture supplied with culture solutions by the continuous flow method are described. The results obtained may be summarized briefly as follows:

When nitrate constituted the sole source of nitrogen there was a continual increase in severity of chlorosis of the plants with each increase in the pH value of the substrate from pH 3.0 to 7.0; at pH 8.0, however, the plants were free from chlorosis.

When both nitrate and ammonium constituted the sources of nitrogen, there was much less chlorosis of the plants than when nitrate alone constituted the source of nitrogen. Plants grown in this series with culture solution of pH values 5.0, 6.0, and 7.0 were free from chlorosis, whereas those grown with solution at pH 3.0 and 8.0 were moderately chlorotic.

When the proportion of anions and the pH value of the culture solution were kept approximately constant, plants grown in the high potassium cultures were slightly chlorotic and those grown in the high calcium and high magnesium cultures were moderately chlorotic. Where the proportions of cations in the culture solutions were held approximately constant, plants grown in solutions high in phosphate and high in nitrate were severely chlorotic, whereas plants grown with solutions high in sulfate were free from chlorosis.

In general, high titrable acidity corresponded with high phosphate content of expressed juices.

An interrelationship between pH value and phosphorus content of the expressed sap is suggested in explanation of iron precipitation and the degree of chlorosis in the plants.

A very close direct correlation was shown between nitrate nitrogen content of the plants and chlorotic intensity.

It is suggested that iron precipitation and the presence of chlorosis are induced in high nitrogen plants by the relatively higher proportions of metabolically active tissue with relatively high pH as compared with the proportion found in low nitrogen plants.

The presence of ammonium nitrogen in the culture medium was associated with a relatively higher phosphorus content and a relatively lower pH value of the expressed sap than was the presence of nitrate nitrogen.

Plants grown with culture solutions containing ammonia were relatively free from chlorosis as compared with plants grown with solutions containing nitrate as the sole source of nitrogen.

REFERENCES

(1) CONRAD, J. P. 1933 Acidity and alkalinity produced by changes in the nitrogen, sulphur, and carbon cycles. *Plant Physiol.* 8: 509–524.

(2) CROZIER, W. J. 1919 Intracellular acidity in *Valonia*. *Jour. Gen. Physiol.* 1: 581–583.

(3) FREE, E. E. 1915 Relative score method of recording comparisons of plant condition and other unmeasured characters. *Plant World* 18: 249–256.

(4) GILE, P. L., AND CARRERO, J. O. 1916 Immobility of iron in the plant. *Jour. Agr. Res.* 7: 83–87.

(5) HOAGLAND, D. R. 1923 The absorption of ions by plants. *Soil Sci.* 16: 225–246.

(6) HOAGLAND, D. R., AND DAVIS, A. R. 1925 Suggestions concerning the absorption of ions by plants. *New Phytol.* 24: 99–111.

(7) HOFFER, G. N., AND CARR, R. H. 1920 Iron accumulation and mobility in diseased corn stalks. *Phytopath.* 10: 56.

(8) HURD, A. M. 1923 Acidity of corn in relation to its vegetative vigor. *Jour. Agr. Res.* 25: 457–469.

(9) INGALLS, R. A., AND SHIVE, J. W. 1931 Relation of H-ion concentration of tissue fluids to the distribution of iron in plants. *Plant Physiol.* 6: 103–125.

(10) JACOBSON, H. G. M., AND SWANBACK, T. R. 1933 Relative influence of nitrate and ammoniacal nitrogen upon intake of calcium by tobacco plants. *Plant Physiol.* 8: 340–342.

(11) JONES, L. H., AND SHIVE, J. W. 1921 Effect of ammonium sulphate upon plants in nutrient solutions supplied with ferric phosphate and ferrous sulphate as sources of iron. *Jour. Agr. Res.* 21: 701–728.

(12) JONES, L. H., AND SHIVE, J. W. 1923 Influence of ammonium sulphate on plant growth in nutrient solutions and its effect on hydrogen ion concentration and iron availability. *Ann. Bot.* 37: 355–377.

(13) LIVINGSTON, B. E., KELLERMAN, K. F., AND CROCKER, WILLIAM 1919 A plan for co-operative research on the salt requirements of representative agricultural plants. Rpt. Com. Div. Biol. Agr. Natl. Res. Council.

(14) LOEHWING, W. F. 1928 Calcium, potassium, and iron balance in certain crop plants in relation to their metabolism. *Plant Physiol.* 3: 261–275.

(15) LOEHWING, W. F. 1930 Effects of insolation and soil characteristics on tissue fluid reaction in wheat. *Plant Physiol.* 5: 293–305.

(16) MASONI, G. 1920 Acidity of plant roots and soil lime. *Staz. Sper. Agr. Ital.* 53: 421–437 (Abs. *Exp. Sta. Rec.* 49: 121).

(17) MATTSON, S. 1930 The laws of soil colloidal behavior: III. Isoelectric precipitates. *Soil Sci.* 30: 459–495.

(18) OLSEN, CARSTEN 1935 Iron absorption and chlorosis in green plants. *Compt. Rend. Lab. Carlsberg, Ser. Chim.* 21(3): 1–51.

(19) OSERKOWSKY, J. 1933 Quantitative relation between chlorophyll and iron in green and chlorotic pear leaves. *Plant Physiol.* 8: 449–468.

(20) PATTEN, H. E., AND MAINS, G. H. 1920 A note on the hydrogen-ion concentration at which iron is precipitated from hydrochloric acid solution by ammonium hydroxide, sodium hydroxide, and hydrogen sulphide. *Jour. Assoc. Off. Agr. Chem.* 4: 233–234.

(21) PETTINGER, N. A., HENDERSON, R. G., AND WINGARD, S. A. 1932 Some nutritional disorders in corn grown in sand cultures. *Phytopath.* 22: 33–51.

(22) ROGERS, C. H., AND SHIVE, J. W. 1932 Factors affecting the distribution of iron in plants. *Plant Physiol.* 7: 227–252.

(23) SESSIONS, A. C., AND SHIVE, J. W. 1928 A method for the determination of inorganic nitrogen in plant extracts. *Plant Physiol.* 3: 499–511.

(24) SHIVE, J. W., AND STAHL, A. L. 1927 Constant rates of a continuous solution renewal for plants in water cultures. *Bot. Gaz.* 84: 317–323.

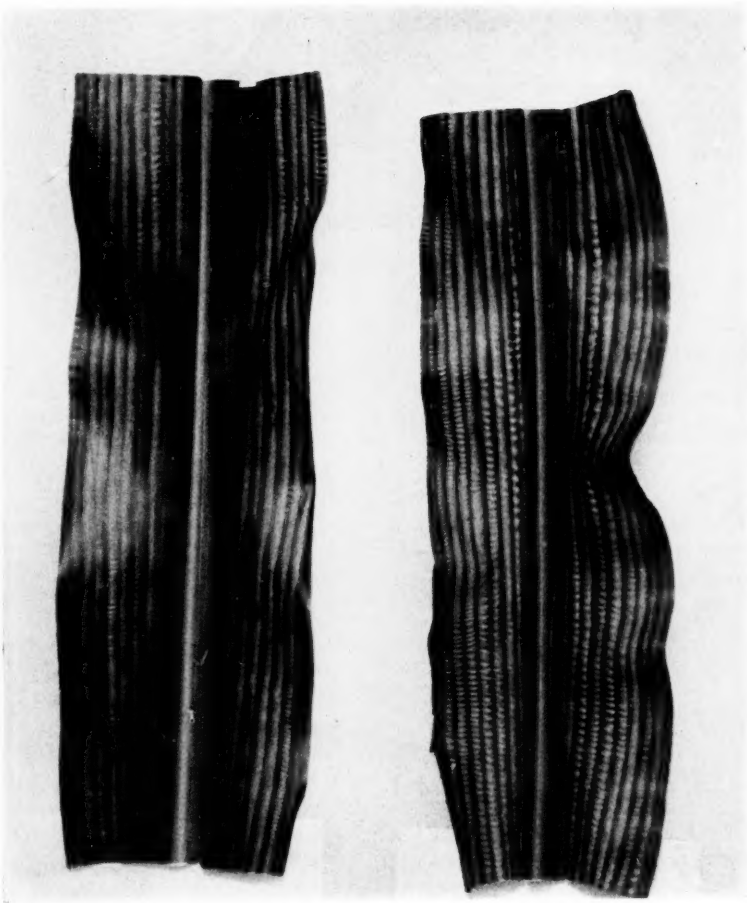
(25) SMALL, J. 1929 Hydrogen Ion Concentration in Plant Cells and Tissues. Borntrager Bros., Berlin.

(26) TIEDJENS, V. A., AND ROBBINS, W. R. 1931 The use of ammonia and nitrate nitrogen by certain crop plants. N. J. Agr. Exp. Sta. Bul. 526.

(27) TRUOG, E., AND MEYER, A. H. 1929 Improvements in the Deniges colorimetric method for phosphorus and arsenic. *Indus. and Engin. Chem. Anal. Ed.* 1: 136–139.

PLATE 1

TYPE OF CHLOROSIS OF CORN ASSOCIATED WITH NONAVAILABILITY OF IRON



WATER-SUPPLYING POWER AND WATER-ABSORBING POWER OF SOILS AS RELATED TO WILTING OF WHEAT AND COLEUS IN GREENHOUSE POT CULTURES[1]

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INTRODUCTION

Water-supplying power and permanent wilting

The water-supplying power of a soil at any specified depth and location may be defined as the dynamic capacity of the soil system to supply water across unit area of an absorber that is in adequate capillary contact with the soil at the given depth (19, 23, 24, 25, 37). The rate at which unit absorbing surface of a plant root may receive water from the adjacent soil is naturally limited by this dynamic soil feature, for water cannot be absorbed more rapidly than it is externally supplied. Water absorption is retarded by environmental soil conditions only when the supplying power of the adjacent soil is inadequate, i.e., when it is less than the corresponding capacity of the absorbing roots; at other times the soil generally exerts no direct retarding influence on the rate of water absorption by plants, that rate being then determined by conditions effective within the plant body (34).

As long as the roots of a plant are growing, the extent and the exact location of the minute surfaces across which water may be absorbed are continuously changing. Since there is no considerable movement of water through the soil excepting when it is relatively very wet (33, 34), this advance of roots into new soil regions is apparently of great importance in connection with water absorption from aerated soils (37). Soon after a newly formed absorptive surface is thus brought into contact with the adjacent soil, it is probable that absorption per unit area is relatively rapid but that, because of drying of the adjacent very thin layer of soil, it decreases rapidly when the initial water-supplying power of the soil was low. The absorption rate also decreases, in any case, with progressive maturation of the adjacent root tissue, for only relatively young root surfaces are generally capable of rapid water absorption. It appears, therefore, that a given absorptive surface of a root system may continue to absorb water without external retardation for a rather long time when the water-supplying power of the adjacent soil was initially great, but when the initial supplying power was not greatly in excess of the absorbing

[1] Botanical contribution from the Johns Hopkins University, no. 141.

power of the given surface, then supplying power may soon decrease until it becomes inadequate. The general soil mass in which a root system is situated dries out more or less rapidly after each wetting, not only because of water absorption by the root system in question, but also because of direct evaporation into the free air and, frequently, because of absorption by competing root systems of other plants.

The first signs of inadequacy in water supply shown by ordinary plants are apt to be retardation of growth and the occurrence of lowered turgor or wilting in some leaves at times of most rapid transpiration. These first symptoms are usually evanescent; a plant showing wilting in the afternoon may recover completely in the succeeding night period. But as the water-supplying power of the soil about the plant roots is further decreased, supposing the daily transpiration rate to remain unchanged, wilting occurs earlier and is more severe each day and recovery therefrom occurs later each night, until the time comes when night recovery fails to occur and dawn finds the plant still wilted because of persisting internal water deficit. The degree of water deficit corresponding to this early-morning wilting generally increases throughout that day, and the plant soon passes into what is called "permanent wilting" if it was not already in that condition at dawn. Recovery from permanent wilting is not possible excepting through addition of water to the soil mass occupied by the root system. Such addition—as by rain or irrigation—quickly increases the very low water-supplying power of the soil mass to a very high value, making it once more abundantly adequate.

What we are calling "permanent wilting" is closely similar to the permanent wilting of Briggs and Shantz (2) and later writers on the relations between soil-moisture content and wilting. Our interest is confined, however, to the dynamic relations of supply and demand, rather than to moisture content or other static soil features. In ordinary plants the onset of permanent wilting in the aerial parts is probably generally closely accompanied by root wilting, or at least by retardation or stoppage of root growth. Loss of root turgor and cessation of root elongation thus occur at a time when effective capillary contact with the adjacent soil and rapid formation of new absorptive surfaces seem to be most needed for the maintenance of health. It is probably for this reason that the rate of water absorption by the plant falls off very rapidly at or about the time of the beginning of permanent wilting—so rapidly that absorption almost ceases at that time.

If drought continues after the beginning of permanent wilting, however, absorption of water by the already seriously injured plant continues at a slow rate, while the plant's water deficit increases rapidly. Meanwhile, the water-supplying power of the soil adjacent to such roots as are still absorbing water naturally continues to decrease—not only because of that slow absorption but also because of absorption by competing root systems and because of direct evaporational water loss. In such a critical period movement of water vapor through the soil and perhaps even the production of water of respiration

(15) in the plant body may be of considerable importance. Without any attempt to consider in this connection various details and various types of plant, it is clear that permanent wilting represents in general a physiological malady that becomes more acute with further progress of the drought period; there are thus many progressive stages of permanent wilting. From none of these stages is recovery possible without addition of water to the soil about the plant roots, but recovery eventually occurs after such addition of water if internal conditions and environmental conditions other than water supply have remained favorable.

The beginning of permanent wilting corresponds to the attainment of a critical low value of water-supplying power in the soil—a value considerably lower than that corresponding to the beginning of visible drought effects in the plant. But the supplying power of the adjacent soil does not decrease at the same rate in the vicinity of all parts of a root system as a drought period lengthens, for the upper layers of soil usually attain the critical supplying-power value and show progressively lower values before the onset of permanent wilting. Also, some parts of the aerial portion of a drought-affected plant may be actually killed by water deficit while other parts are still turgid and growing. And the internal limitations of a plant, combined with high evaporation, may bring the foliage to death by drought even when the environmental water-supplying power is very great (14). It is obvious that a truly satisfactory criterion by which a suitable plant may be judged to have just attained permanent wilting is somewhat difficult to fix upon, as has been noted by many writers. Nevertheless, many useful studies on the relation of the beginning of permanent wilting to soil-moisture conditions have been carried out by a number of investigators, some of whom have dealt with water-supplying power (19, 22, 23, 24, 25, 36, 37) while others have dealt with water content of the soil (1, 2, 3, 19, 32, 34) or soil suction (5, 6, 10, 11, 21, 27, 30, 31), both of which are static features.

In most of the experimentation thus far carried out on the beginning of permanent wilting the plants used have been of ecological types such that the advance of wilting may be observed visually, and the plants have been grown in pots or other limited soil containers in a greenhouse. In such experiments the plants are first grown to suitable size with adequate water supply, and then addition of water to the soil mass is discontinued. When permanent wilting is judged to have begun, the soil-moisture condition is measured, and the result of that measurement is taken to represent approximately the critical soil-moisture value which corresponds to the onset of this phase of wilting. Our experiments were of that sort, but wilting and the drying of the adjacent soil were allowed to advance somewhat beyond the onset of permanent wilting, as will be seen.

To study the decrease in water-supplying power of the soil about the roots of a plant as a drought period advances, or to obtain quantitative measures of supplying power corresponding to any stage of wilting (such as the beginning

of permanent wilting), it is, of course, necessary that the instrument employed should be located within the soil region occupied by the roots—so that the supplying-power values may correspond approximately to an average condition of moisture supply to which the plant is subjected. For deeply rooted plants it is desirable to apply tests at several different soil depths. For example, Wilson (36) found that *Achillea millefolium* (yarrow) in a lawn remained green and vigorous long after neighboring shallow-rooted grasses had become thoroughly dry and brown on account of drought.

Water-supplying power—which represents the rate at which the soil system is able to deliver water across a sectional surface—is naturally to be measured as a time rate with reference to a standard areal unit, and initial supplying power may be taken to represent the average rate for a standard initial period following the beginning of absorption. Measurements are conveniently stated as grams (or milliliters) of water delivered to a suitable absorber ("artificial root") per hour, in the first hour of absorption. It appears, for example, that *Poa pratensis* (Kentucky bluegrass L.) in a lawn maintained vigorous growth in the summer at Baltimore as long as the soil about it, at a depth of 5–7 cm., showed an initial water-supplying power greater than about 8 mgm./sq.cm./hr., and that the leaves were all dead by the time this value had decreased to about 4 mgm./sq.cm./hr. (36).

To obtain such measurements directly it is necessary to employ an instrumental absorber that is capable of removing water from the adjacent soil more rapidly than water is supplied, throughout the first hour of application. Pulling and Livingston (25) and Pulling (24) used osmotic cells with valuable preliminary results. They found that the soil of a pot in which a plant of *Phaseolus vulgaris* (navy bean) had attained permanent wilting, with very low air humidity, showed initial water-supplying power of about 3 mgm./sq.cm./hr. Although the osmometer method is probably capable of improvement, all soil osmometers thus far tried have been somewhat difficult to prepare, standardize, and maintain.

Up to the present time, the most satisfactory method for estimating the water-supplying power of soil is based on the employment of dry soil-point cones of porous porcelain (19, 36), which are thrust into the soil and left in contact with it for an hour or less, the amount of water absorbed being ascertained by weighing. Although these instruments have given excellent results whenever tried (4, 7, 8, 20, 36), this general method will probably be further improved. Mason (23) and Hardy (7, 8) used wooden cones (lead pencils). Soil-point cones were employed in the experiments described in the present paper.

Water-absorbing power of the soil and absorption pressure

The water-absorbing power of a soil at any specified depth and location may be defined as the dynamic capacity of the soil system to remove water by capillary absorption across unit area, from an adequately maintained

source of water supply. For any soil mass this power increases as the soil becomes drier, and conversely. It bears no direct relation to water absorption by plant roots but it is obviously dependent—to a great degree at least—upon static features that are effective in determining water-supplying power and it is an interesting soil characteristic in other ways.

One of these static features may be termed the "water-absorption pressure" of the soil, its "capillary potential" or its "capillary-pressure deficit"—the hydrostatic-pressure gradient that induces mass water movement from a surface of continuously adequate water supply into the adjacent soil. This pressure may represent the resistance offered by the soil to water absorption by a soil-point cone or other absorber. Its logarithm has been called "pF" by Schofield (31). It might be measured more or less satisfactorily by employing suitable osmometers with pressure gages attached, as was first suggested by Whitney and Cameron (35), but such a method would be difficult and tedious and it has never been seriously tested, so far as we know. By this means one of us (12) found that a clay soil with a moisture content of 15 per cent withdrew water from a 1.5 *M* sucrose solution in a Pfeffer osmotic cell, while the same solution took water from the soil when the latter had a water content of 25 per cent. When the experimental soil had a water content of 20 per cent, its water-absorption pressure was apparently about equal to the osmotic value of 1.5 *M* sucrose solution—about 54 atmospheres. Such a value seems to be altogether too great, and the osmometer method seems to be at best no better than somewhat promising.

Another method for estimating the capillary-pressure deficit of soils has received more attention and has recently been used with satisfactory results for soils the absorption pressure of which is not too great. A hollow porous-porcelain cylinder or cone is permanently buried in the soil at the desired depth. It is permanently filled with water, and the suction pressure developed by soil absorption is measured from time to time by means of an attached pressure gage or manometer. One of us began to study the performance of such suction-manometer devices in 1908; that study has been continued from time to time, with varying details of construction and in the hands of a number of students here and at the Desert Laboratory, but possibilities for improvement always seemed greater than actual performance and suitability for general use. In recent years instruments of this type have been developed and applied by Rogers (28, 29, 30), by Richards and Gardner (26, 27), and by others and they bid fair to be very useful within their limitations.

Although instruments of this sort—tonometers, tensiometers, moisture meters, or whatever they are called—may be permanently placed in the soil at any requisite depth and may be read easily from time to time without further disturbing of the soil—a prime desideratum in an instrument for measuring soil-moisture condition—they are thus far not wholly satisfactory, for the following reasons: (*a*) they give data on absorption pressure rather than on supplying power, (*b*) they require special attention because of undis-

solved gas, which is apt to appear within them, and (*c*) they regularly fail to operate when the pressure to be measured is greater than about 60 or 65 cm. of mercury column. The last-mentioned difficulty is serious because that degree of suction is shown by clayey soils while ordinary plants rooted therein do not show very serious drought effects. For example, although a sand suction of a very few centimeters of mercury column sufficed to bring plants of *Vicia faba* to their death from drought, plants of the same kind failed to wilt badly (although growth was retarded) with clay suction of 60 cm. Similar results have recently been recorded by Rogers and others. It is thus obvious that the internal surface of the soil, or some related soil feature, needs to be taken into account when an attempt is made to relate soil suction to plant growth. It is equally clear that a generally satisfactory method for estimating absorption pressure should be applicable to all kinds of soil at the onset of serious wilting and therefore should show pressure-deficit values much greater than the natural limit of suction, which is about 76 cm. of mercury column. It seems likely, for instance, that plants of Vicia in clay soil might not become seriously wilted through drought until the water-absorption pressure of the soil about the roots had increased to a magnitude much greater than 76 cm. of mercury column. Such a manometer reading would of course be the sum of two quite different terms, one of which would represent the maximal limit of true suction under the circumstances, while the other would represent true negative pressure, due to traction—as in the familiar Askenasy experiment. It seems probable that porous tonometers for soil studies may eventually be developed which will register up to several hundred centimeters of mercury column, but this statement may be too hopeful; it is now relatively easy to make tonometers that show traction pressure in water and mercury of 50 cm. or more (in addition to maximal suction), but no one yet appears to have succeeded in applying these instruments to the soil. That has been attempted several times in this laboratory, both with water and with other liquids, but thus far the results have been unsatisfactory. Nevertheless, this type of instrument is more satisfactory for the study of soil-moisture condition than any other thus far developed in which the soil is not necessarily disturbed to some extent whenever a reading is to be taken.

Turning again to the water-absorbing power of the soil, the development of porous-porcelain cones for estimating water-supplying power naturally led to the suggestion that water-absorbing power might be estimated in terms of the rate of water movement into the adjacent soil from an adequately wet surface of known area. Arrangements similar to the Livingston auto-irrigator (13, 18), with short-column mercury barostat to prevent excess hydrostatic pressure within the porous-porcelain piece, were tried as early as 1905, at the Desert Laboratory, but these instruments maintained a nearly uniform rate of water loss throughout the increasingly arid period of the Tucson fore-summer drought; it appeared that a slowly decreasing volume of soil

surrounding the continuously wet porous-porcelain piece was maintained at an approximately fixed average moisture content and that this wet volume of soil decreased as the surrounding soil dried out, the rate of water movement from wet porcelain to soil being approximately maintained. So far as we know, this type of instrument has not yet been seriously studied, although it may well be worthy of modification and further test, at least with reference to some features of the soil-moisture problem.

This device resembles the tonometer type for estimation of suction pressure in that the porous-porcelain piece remains permanently in the soil at the specified depth and is kept filled with water at all times, but the barostat resistance to water loss into the soil remains constant and does not increase as water continuously moves outward. The time rate of water absorption by the soil is recorded from time to time in terms of the rate of water loss from a suitably graduated reservoir, such as a burette. For this type of instrument—as well as for the tonometer type and for our new device, described below—it is desirable that the porous-porcelain member be conical, with the cone base horizontal and below, rather than cylindrical; thus the more or less continuous movement of soil particles tends always to settle the soil firmly against the porous surface, which is not always true of the whole periphery of a cylinder, whether the latter be vertical, horizontal, or oblique (13). In some respects a plane horizontal porous plate, facing upward is even more satisfactory than a cone.

It should be added that this continuously operating device is exceedingly useful in experimentation with plants grown in pots or other containers that confine the root system to a constant volume of soil. In such cases the average moisture content of the soil mass is maintained constant, and the fluctuating rate of water loss from the reservoir reflects corresponding fluctuations in the rate of removal of water from the soil. If evaporation at the free soil surface is prevented or kept nearly constant at a very slow rate, fluctuations in the rate of water loss from the irrigator may be taken to represent corresponding fluctuations in the water-absorbing power of the root system—which generally depends largely on aerial evaporativity as it influences transpiration; this aspect of the general problem of plant water relations was considered rather extensively by Livingston and Hawkins (17), whose experiments were carried out with porcelain cylinders, before irrigator cones had become available. In this connection reference may also be made to a paper by Livingston, Hemmi, and Wilson (18), in which both soil suction and water-supplying power are considered. (See also Kramer, 11a.)

While studying in this laboratory (1923–1925), and at the suggestion of one of the present authors, Prof. Ichiro Ohga, of Tokyo, carried out a short series of tests with an auto-irrigator device that was applied to the soil only temporarily, at times of observation, when the rate of water absorption by the soil was ascertained for a short initial period. The instrument consisted essentially of a Livingston soil-point cone filled with water and connected

to a small burette, with a mercury barostat between burette and cone. A portion of the supply tube was of flexible rubber, so that the cone might be thrust into the soil to be tested, a suitable opening having first been made when necessary, by means of a dibble. While the instrument was in position, water moved from wet porcelain to surrounding soil at a rate depending on the current water-absorbing power of the soil, but the instrument was removed after each short exposure. Although the results obtained were very satisfactory and this instrument seems to offer much promise, no account of these tests was published, for it seemed desirable to develop the concept of water-supplying power further before introducing the related but more complex concept of water-absorbing power. Nevertheless, that little instrument used by Professor Ohga remains worthy of improvement and serious study. Like the soil-point cone, it is logically good, at least in that it furnishes measurements of a dynamic rather than of any static soil feature, but it was not left permanently in the soil, and its insertion, for each observation, naturally involved some compression of the soil, just as when a soil-point cone is inserted for estimating water-supplying power.

It was soon suggested that these undesirable characteristics might be avoided if a porous-porcelain cone, permanently buried in the soil at the requisite depth and equipped with graduated reservoir and barostat, were filled with water only during short periods of observation, when rates of outward movement of water might be measured volumetrically. The new instrument brought forward in the present paper is based on that suggestion.

Unlike the tonometers previously mentioned, this instrument furnishes no measure of static pressure differences; its readings represent initial rates of water absorption by the soil. Such rates are of course conditioned not only by the current capillary-pressure deficit of the liquid phase of the soil but also by the resistance of the adjacent soil to water movement, by the internal characteristics of the instrument itself, by the viscosity of water (as the latter varies with temperature), and by the length of the standard time period employed for observations. Although tonometers designed to measure pressure deficit fail whenever that deficit is greater than about 60 cm. of mercury column, as has been mentioned, our new device has no such limitations. Like Pulling's interesting and instructive, but not yet practical, osmometric device (24) for measuring water-supplying power, the new instrument may be buried or "planted" in the soil at any desired depth and left there indefinitely, readings being taken at desired intervals. The soil about the porous-porcelain member may be allowed to settle and attain its natural state of packing before readings are begun. Although obviously susceptible of further refinement and improvement, it proved to be remarkably satisfactory in our tests. Its main defect appears to lie in the fact that it measures absorbing power rather than supplying power, but it may be that the former may furnish useful indices of the latter. It is to be remembered, however, that water-supplying power of the undisturbed soil is clearly the

dynamic feature with which students of the subterranean water relations of plants should be primarily concerned.

As new concepts emerge and as new instruments are devised, terminology inevitably becomes increasingly difficult. If our new instrument sustains its apparent promise it may eventually need a simple name, but a satisfactory one does not readily suggest itself, for the few Greek or Latin roots that might logically be called into use here have already been greatly overworked, with consequent confusion and ambiguity. For the present we may cling to plain English and call this device our "water-absorbing-power meter for soils," hoping that these hyphens may be allowed to stand; or we may term it our "irrigator device for estimating water-absorbing power." Other types of water-absorbing-power meter that have been described in the literature, so far as we know, are those of Livingston and Hawkins (39), Pulling and Livingston (40), and Pulling (41), which have already been mentioned. The new instrument is, of course, to be sharply distinguished from soil tonometers (which give measurements of pressure gradients or deficits) and from water-supplying-power meters such as the Livingston soil-point cone. Additional members of each of these families will probably appear as the study of subterranean water relations of plants goes forward.

It should be added that, as far as we are aware, suitable methods and devices for estimating water-supplying power and water-absorbing power of the soil when air temperature is below 0°C. remain to be developed. On the other hand, Rogers (30) has developed his tonometer for soil suction for use in freezing weather, employing an ingenious arrangement somewhat similar to the one used by Livingston and Haasis (16) to prevent injury from freezing in porous-porcelain atmometers.

EXPERIMENTATION

Soil mixtures

Sixteen different soil mixtures were employed in these experiments. They were prepared by mixing clay loam, humus (muck), and sand in as many different proportions by somewhat roughly measured volume. The different sets of proportions used are shown by the coördinates of the circles on the triangular diagrams of figures 1 and 4, the sum of all three coördinates being 15 in every instance.

The percentage water-holding capacities of these mixtures were ascertained by means of cylindrical pans of the Hilgard (9, p. 208) type (1 cm. deep and with bottom area of 100 sq. cm.). In these measurements the soil was allowed to fall into the pan from a horizontal sieve 30 cm. above the pan bottom, the pan wall being temporarily extended upward 5 cm. by means of a removable cylindrical ring of sheet metal. Soil was added till the ring was heaping full, when the ring was lifted slightly and the lower 12 mm. of soil was cut off by means of a thin metal plate sliding on guides. Thus the pan was over-filled to a height of 2 mm. After the soil of a pan had been

saturated with water from below and after drainage had ceased, the surplus soil was struck off by means of a straight edge and the water content of the resulting 1-cm. column of soil (containing 100 cc.) was ascertained by weighing, drying, and reweighing. Water-holding capacities were computed as

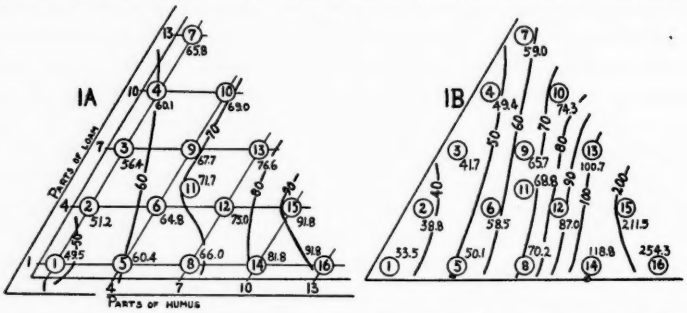

FIG. 1. DIAGRAMS SHOWING VOLUMETRIC PROPORTIONS OF LOAM, HUMUS, AND SAND IN SIXTEEN DIFFERENT SOIL MIXTURES, WHICH ARE NUMBERED SERIALLY IN ASCENDING ORDER OF THEIR WATER-HOLDING CAPACITIES, THE CAPACITY PERCENTAGES BEING INSCRIBED, WHEREAS THEIR DISTRIBUTION IS SHOWN BY CONTOURS

Part A shows capacities based on soil volume and Part B shows them based on dry weight

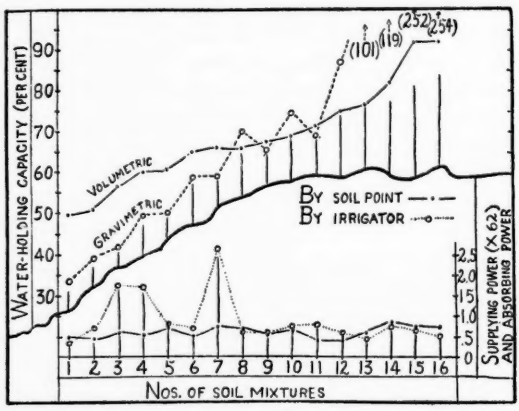

FIG. 2. UPPER PART, GRAPHS SHOWING WATER-HOLDING CAPACITIES OF THE SIXTEEN SOIL MIXTURES SPECIFIED IN FIGURE 1. LOWER PART, GRAPHS OF AVERAGE SOIL-POINT ABSORPTION (× 62) AND AVERAGE IRRIGATOR LOSS WHEN PLANTS WERE BADLY WILTED

All values in grams

grams per 100 cc. of soil volume and per 100 gm. of dry soil. The resulting percentage values of volumetric water-holding capacity and the corresponding values of gravimetric capacity are inscribed on the diagrams of figure 1, A and B, where contours indicate the distribution of high, intermediate, and low values. The numerals in circles are the numbers of the soil mixtures, which

follow the ascending order of the volumetric capacity percentages. The water-holding capacities are also shown by the graphs of the upper part of figure 2.

Both diagrams, as well as the graphs just mentioned, show greatest capacity for the mixture highest in humus content (no. 16) and least capacity for the mixture highest in sand content (no. 1), with a fairly regular gradation between these extremes. In the upper part of figure 2 the graph for the volumetric values ascends regularly to the right simply because the soil mixtures were numbered in the ascending order of these values. Only the gravimetric percentages extend above 100, which illustrates and emphasizes the long-familiar observation—which seems still to be unappreciated by many writers—that the volume basis is the only logically satisfactory one for use in computing soil-moisture contents when the latter are to be employed in studies of plant water relations, especially when the soils dealt with contain much organic matter. Plant health is certainly not at all dependent on the specific gravity of the solid phase of the soil mass occupied by the root system but it is obviously dependent in large measure on the volume of that soil mass, for all water absorbed must be taken from that volume of soil and from nowhere else.

Pots and irrigator cones

The prepared soils were placed in 10-inch pots of usual form, two porous-porcelain irrigator cones of the Livingston type (13) being "planted" side by side in each pot, with their horizontal bases 9 cm. above the pot bottom (fig. 3, A). The plane surface and the neck of each irrigator were waterproofed externally with spar varnish, the conical portion of the instrument (approximately 100 sq. cm.) being smooth-ground and uncoated (fig. 3, B). Each irrigator was furnished with a rubber stopper bearing two tubes of block tin (outer diameter, 6 mm.; bore, 3 mm.), each of which terminated a few centimeters above the soil surface, where it bore a short rubber tube and a tubing clamp. One tin tube extended downward to the bottom of the irrigator, and the other ended below at the lower face of the stopper. The soil was about 25 cm. deep in each pot, and the porous conical part of the irrigator (about 6 cm. high) was thus from about 9 to about 15 cm. below the free soil surface and about the same distance above the pot bottom. These irrigator cones have an external diameter of about 7.5 cm. at base, and the cylindrical neck is about 2.5 cm. in outer diameter and 4 cm. high. As the soil about the instrument shifts with changes of temperature and moisture condition it tends to settle against the conical surface, thus maintaining good capillary contact between soil and porous porcelain, as has been noted.

Wilting

About a hundred wheat grains were planted in each pot, along with two vigorous coleus plants, grown from cuttings. After the wheat seedlings

appeared, some were removed so that those remaining were 2–3 cm. apart. The cultures stood in an east-west row on a greenhouse bench, being watered from day to day in the ordinary way, and the plants grew vigorously. Each pot received one watering of a balanced nutrient solution when the study was about half completed. When the wheat plants were about 10 cm. tall, watering was discontinued and the soil masses were allowed to dry out gradually, till the plants were badly wilted in the evening and failed to recover before the following morning. Then the soil tests described below were made.

The stage of wilting thus characterized—which represents somewhat more severe drying out of both plants and soil than is represented by the onset of permanent wilting—was attained on the same day by both kinds of plants in any pot. No attempt was made to ascertain the exact hour when permanent wilting really began. After its beginning the plants must have continued to remove water from the soil adjacent to their roots at a relatively slow rate, and loss of soil moisture through the pot wall and by evaporation from the free soil surface naturally continued also. When the plants were found to be wilted in the morning (having wilted on the preceding day and not having recovered in the night) the soil adjacent to the roots and that near the free surface above were therefore certainly somewhat drier than they had been on the previous day at the time of the onset of permanent wilting. It should also be noted that several pots were sometimes ready for test on the same morning, in which case it was unavoidable that some should be tested sooner than others, because of the time consumed in setting the soil instruments and obtaining readings from them—only one pair of hands being available for those operations. It sometimes happened, therefore, that one pot received attention early in the forenoon and another could not be tested till afternoon. Consequently our soil tests were generally applied when the soil mass in question, especially in its upper region, was drier than it should have been to correspond to the first attainment of permanent wilting by the corresponding plants.

Tests of water-absorbing power

When a soil mass was to be tested, one of its two irrigator cones and the attached tubes were completely filled with water through the longer tube, and the upper end of that tube was attached to a burette of water above, the shorter tube being closed with a clamp. The system was allowed to stand for a 10-minute adjustment period, after which was recorded the volume of water removed from the burette in the succeeding hour. To counterbalance the excess of hydrostatic pressure due to the water meniscus in the burette being above the level of the buried irrigator and to introduce a standard pressure resistance to soil absorption, a U-tube barostat with a 9-cm. column of mercury regularly intervened between burette and irrigator tube. Without the barostat, excess of hydrostatic pressure in the cone would have amounted to about 5 cm. of mercury column. Movement of water from instrument

to soil took place only by capillary suction, with a driving pressure of about 72 cm. As soon as one of the irrigator cones was in operation the second instrument of the same pot was filled and started in the same way, with a second burette, so that both were operated almost simultaneously—each for 1 hour subsequent to its 10-minute adjustment period. When these readings were completed the burettes were disconnected and the porcelain pieces were emptied by application of suction through the longer tube, the clamp of the shorter one being open. The two resulting simultaneous irrigator readings from the same pot were averaged and the resulting primary average was recorded as an approximate measure of the current initial water-absorbing power of the soil mass in question, at the 9–15-cm. depth.

Tests of water-supplying power

Along with the two irrigator readings just referred to, two readings were also made by means of Livingston soil-point cones. The soil-point cone is a hollow porous-porcelain piece with wall about 3 mm. thick and with a cylindrical neck about 2.4 cm. in external diameter and 2.5 cm. high, which is open at the top and continuous below with a conical part about 5 cm. high that ends in a point. The whole is externally waterproofed excepting for an absorbing zone 2 cm. high on the conical surface. In operation, these cones were thrust vertically into the soil so that the edge of the neck was in each instance even with the free soil surface (as indicated in fig. 3, A) and the absorbing zone (about 12 sq. cm.) was from 5 to 7 cm. below the free soil surface. Two cones (previously dried over $CaCl_2$) were used simultaneously for each pot, being inserted about 5 cm. apart and about midway between the center of the free soil surface and the pot rim. For the firmer mixtures a 1-cm. cylinder of soil was removed with a cork-borer, to a depth of about 5 cm., before the instrument was inserted and pressed into position. In such cases the soil that had been removed was finally crumbled and returned, to fill the hole left when the instrument was lifted; in other cases no soil was removed, and the holes left by the soil-point cones were filled by merely loosening and shifting the slightly compressed soil of the immediate vicinity. The cones were left in the soil for the standard period of 1 hour, and the weight of water absorbed by each in that period was ascertained by weighing, in the usual manner. The two readings from each test were averaged, and the resulting primary average was recorded as an approximate measure of the current initial water-supplying power of the soil mixture in question, for the 5–7-cm. depth.

Repeated wiltings

At the end of these operations, when two irrigator readings for the 9–15-cm. depth and two soil-point readings for the 5–7-cm. depth had been made, when the irrigator cones had been emptied and when the small holes resulting from the insertion of the soil-point cones had been filled, the wilted plants

were thoroughly watered and allowed to recover and continue their growth. When they were once more vigorous, watering was again discontinued, wilting like that already described was allowed to supervene, and the procedures just described were repeated. A soil-point cone was never applied where one had been applied in an earlier test. The plants of each pot were thus wilted five times, with growth intervals between successive wiltings, this entire study being completed in the period from January to June, 1934. The length of the drying-out period varied between 9 and 30 days.

Computations

For each soil there were available five primary irrigator averages and five primary soil-point averages, one for each kind of instrument for each test. Each set of five corresponding primary averages was averaged to give a secondary average for the soil mixture in question, representing all five tests together. There were thus finally available for each of the sixteen mixtures a single secondary average from soil-point readings and a single one from irrigator readings.

The general background or frame of these experiments

The primary averages just mentioned were all to represent soils in which the plants had just attained a critical stage of advanced wilting; i.e., the plants had become so severely wilted on the day before a test that they had not recovered in the following night period. At the times of test, however, as has been said, wilting had advanced, and the soil had dried, considerably beyond the stage that would have represented the onset of permanent wilting. Naturally the whole soil mass was never uniform in water content or in water-supplying or water-absorbing power. For any mass of soil that remains undisturbed, water-supplying power across any sectional area decreases as the water content of the soil adjacent to that sectional area decreases, through plant absorption and as a result of evaporation; and the water-absorbing power increases correspondingly. Our pots of soil lost water laterally, through their more or less porous walls, as well as by direct evaporation from soil to air and by plant absorption, and the wilting plants served as indicators concerning only the mean water-supplying power of the soil adjacent to their absorbing root peripheries. Thus, when the tests were applied to a pot its soil was drier (*a*) close to the absorbing roots, (*b*) adjacent to the pot wall, and (*c*) near the free soil surface than it was elsewhere; in general its moisture content, and consequently its water-supplying power, were greater toward the middle and bottom of the mass than near the free surface. On this account it is important to bear in mind that our supplying-power values refer to the 5–7-cm. depth, whereas our absorbing-power values refer to the 9–15-cm. depth. The exposure of the irrigators was therefore much more nearly like that of absorbing root surfaces than was the exposure of the soil-point cones.

It was consequently to be expected that our irrigator readings would be

slightly greater, and that our soil-point readings would be much smaller, than they should be to represent soil close to the absorbing roots at the beginning of permanent wilting. If these had been ordinary pot cultures the soil adjacent to the soil-point cones (at the 5–7-cm. depth) would naturally have been drier than that adjacent to the absorbing roots, and that difference was surely accentuated in these experiments because the two empty irrigator cones intervened between the deeper and moister portion of the soil mass and the drier surface layer, in which the soil-point cones were applied; the presence of the irrigators must have retarded water movement from the bottom of the pot toward the free surface during the drought periods.

Furthermore, since the several tests with each pot were consecutive—with periods of watering and growth intervening—the plants were older and larger, with increasingly more extensive root systems, as the experiments proceeded. And the climatic conditions of our greenhouse room altered considerably—especially with reference to light conditions—from late winter, when the first wiltings occurred, to early summer, when the study was discontinued. The wilting periods were somewhat shorter for the first series of tests, when the greenhouse was artificially heated, than for subsequent series. But the instrument readings showed no consistent variation with respect to the advance of the season, as will appear subsequently. Flowering of coleus was prevented by removing the flowering shoots as soon as they became evident.

Other important background features of this series of experiments are related to the barostat resistance of the irrigator device and the comparative areas of the two instruments. The manner in which the rate of water loss from a porcelain instrument of this sort is controlled by the extent of the area of contact and by the barostat resistance employed, in conjunction with the water-absorbing power of the adjacent soil, calls for special study at some later time. An important characteristic of our irrigator device was its internal hydrostatic pressure (about 72 cm.); in an arrangement of this sort, the height of mercury column employed in excess of the barostat column required to counterbalance the water column influences to a very marked degree the rate of water absorption by the adjacent soil. That excess was 4 cm. of mercury column. An excess resistance of 10 cm., which was tried in a few tests, gave very unsatisfactory and irregular results, but no special attention was given to the important subject of hydrostatic resistance to soil absorption.

Finally, it should be noted that the 1-hour period of exposure for the soil-point cones and the like period for the operation of the irrigators, along with the preceding 10-minute period for irrigator adjustment, are additional constants in the frame of this study. Experience has shown the 1-hour period for soil-point tests to be practically as well as theoretically quite satisfactory when the water-supplying powers in question are not excessive. But the experiments now reported are the first to be carried out for quantitative estimate of water-absorbing power with the sort of irrigator device here employed, and we simply used the same length of period for both in-

struments. The adjustment period for the irrigators was introduced additionally because that instrument does not begin to operate consistently as a water-supplying system immediately on being filled; some little time elapses before the porous wall becomes thoroughly impregnated with water. It is to be expected that further studies concerning all these various constants of experimentation may result in valuable improvements in this sort of technique or in still more satisfactory methods.

Numerical results

Because irrigator readings were generally about 62 times as great as the corresponding soil-point readings, all soil-point values (expressed in fractions of a gram) were multiplied by 62. Consequently, the result may be considered the same as though each reading had represented a total amount of

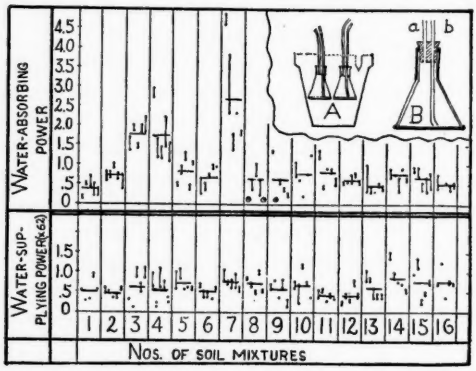

FIG. 3. GRAPHS SHOWING BY DOTS INDIVIDUAL SOIL-POINT READINGS OF WATER-SUPPLYING POWER (× 62); ALSO ACTUAL IRRIGATOR READINGS OF WATER-ABSORBING POWER
Averages are shown by bars. All values in grams

absorption by 62 soil-point cones similarly exposed. The resulting multiple soil-point values have the same general order of magnitude as that shown by the actual irrigator readings for most of the soil mixtures, and it thus becomes feasible to plot both series of values to form directly comparable graphs. The actual soil-point values will also be considered.

The main part of figure 3 presents all the multiple readings of soil-point cones and all the actual readings of irrigators, both being expressed in grams, although irrigator readings were, of course, actually volumetric—in milliliters. Each of these values is represented by the ordinate of a dot, and the two dots for each pair of simultaneous readings are joined by a vertical line. In some instances the two dots coincide and so appear as one. The five consecutive tests for each soil are represented from left to right in each case. Primary-average values are represented by the middle points of the vertical lines or by the dots when these appear singly. Secondary averages,

representing all five tests taken together, are shown by the ordinates of horizontal bars, one of which appears for each kind of instrument, for each soil mixture. Three exceptionally low pairs of irrigator readings (about 0.1 gm.) were omitted in computing the secondary averages; these are represented by circled dots (soil mixtures 8 and 9).

These graphic representations of our numerical results are superior to tabulation in that they present the whole story of numerical deviation or variability at a single glance. From them it is seen that the reading deviations are generally remarkably small, with the exception of the irrigator readings for mixtures 4 and 7, for which unusually great deviation is shown. There is obviously no consistent relation between direction and extent of reading deviation and time of test; therefore, each secondary average may be taken to represent the soil mixture in question for all five wiltings. These values (ordinates of horizontal bars in figure 3) show no pronounced deviation

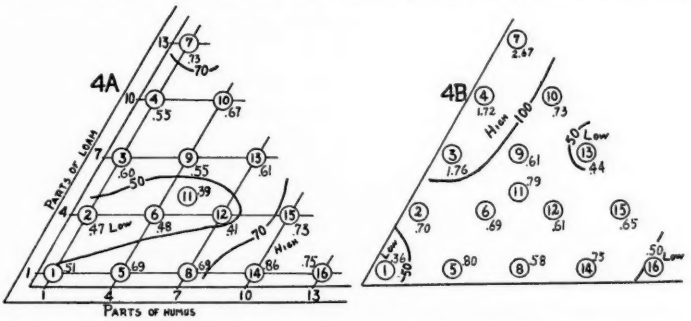

FIG. 4. PART A, DISTRIBUTION AMONG SIXTEEN SOIL MIXTURES OF AVERAGE SOIL-POINT VALUES (× 62). PART B, DISTRIBUTION OF AVERAGE IRRIGATOR VALUES
All values in grams

from mixture to mixture, excepting mixtures 3, 4, and 7 in the irrigator series, the secondary averages of which are unusually great. And the secondary averages from soil-point cones and irrigators are all very similar when these three exceptions are disregarded. Finally, there is no notable relation in either series between these secondary averages and water-holding capacity—when it is borne in mind that the soil mixtures are numbered in the ascending order of their volumetric capacity percentages.

The secondary averages are presented more simply, without their deviations, by the two linear graphs shown in the lower part of figure 2. Comparison of these graphs with those for water-holding capacity (upper part of the same figure) fails to bring out any notable consistency between water-holding capacity (on either volumetric or gravimetric basis) and either water-supplying power (soil-point data) or water-absorbing power (irrigator data). The supplying-power graph appears to represent a horizontal line throughout, with ordinate of 0.61 gm., and the same thing is true of the absorbing-power

graph if the points for soils 3, 4, and 7 are disregarded. Furthermore, there is no apparent relation between average absorbing power and water-holding capacity for any of these three apparently exceptional soil mixtures.

Apparent relations of secondary averages to soil composition

Although the graphs of figures 2 and 3 fail to show any consistent relations of either soil-point values or irrigator values to water-holding capacity, yet some notable relations become apparent when the secondary averages are plotted on triangular diagrams, as in figure 4. But these two diagrams are in pronounced disagreement. The triangle of multiple soil-point averages (fig. 4, A) shows soil mixtures 11 and 12 as giving exceptionally low values (0.39, 0.41 gm.), whereas mixture 14 is shown as giving an exceptionally high value (0.86 gm.). On the other hand, the triangle of irrigator averages (fig. 4, B) shows an exceptionally low value for mixture 1 (0.36 gm.) and very high values (far above 1.00 gm.) for mixtures 3, 4, and 7, which are the three exceptional mixtures previously mentioned.

The apparent relations between soil-point values and soil composition that are shown by figure 4, A may or may not be significant; at any rate, their implications are not easy to understand. On the other hand, the relations of the three exceptionally high irrigator values to soil composition can hardly be regarded as accidents of experimentation, even though two of them (for mixtures 4 and 7) do represent exceptionally wide irrigator deviation. There can be no doubt that mixtures 3, 4, and 7 did actually exhibit excessively great water-absorbing power at the 9–15-cm. depth. These mixtures may be characterized as having (*a*) very low humus content (1/15), (*b*) from intermediate to very high loam content (7/15–13/15), and (*c*) from very low to intermediate sand content (1/15–7/15). Mixture 7, which gave the very highest irrigator value, would probably have been called a clay soil by most gardeners. It may be supposed that the common peculiarity of these three mixtures was in some way related to amount and distribution of colloid material. Perhaps it may have been related to peculiar characteristics of the plant root systems developed in these mixtures. Available information is far too meager to justify an attempt at theoretical discussion of these three strikingly peculiar irrigator values at this time, but it may be recalled that clayey soil has been found—by students in this laboratory as well as by Rogers (30)—to develop exceedingly great suction pressure (60 cm. or more, of mercury column) without the occurrence of marked drought effects in the indicator plants. In that connection it seems important to remark that figure 4, B, shows no consistent relation between water-absorbing power of the soil and relative clay or colloid content, excepting that mixture 7, with maximal absorbing power (2.67 gm.), also had maximal loam content (13/15, by volume).

Grand averages for the several tests and for all tests

Because the two graphs of the lower part of figure 2 are both essentially coincident horizontal lines (excepting the points for soil mixtures 3, 4, and 7, with regard to irrigator loss) it is desirable to examine the grand averages that may represent the water-supplying power of all sixteen soils taken together and the water-absorbing power of the thirteen of them that nearly agreed in that respect. We may first consider the five separate series of tests for which these averages are as follows:

	SOIL-POINT ABSORPTION (×62); AVERAGE FOR 16 MIXTURES	IRRIGATOR LOSS; AVERAGE FOR 13 MIXTURES
	gm.	*gm.*
1st test	0.71	0.72
2nd test	0.63	0.58
3rd test	0.54	0.65
4th test	0.63	0.53
5th test	0.52	0.62
Ave., all tests	0.61	0.62

The close similarity among the averages for the separate tests adds emphasis to the conclusion that the variability of our data was not related to time of test, age of plants, etc.; all these values are surely as nearly alike as might be expected from experimentation of this sort.

In the lower part of figure 2 the average ordinate for the entire soil-point graph and that for the irrigator graph (with the three unusually high points omitted) are alike, being represented by the two final averages just given (0.61 and 0.62 gm.). The device of multiplying all soil-point values by 62 made it feasible to present the graphs of figures 2 and 3 in comparable fashion, for studying the relation between water-holding capacity, on the one hand, and supplying power and absorbing power, on the other hand. But for further comparison of soil-point values with irrigator values it is desirable to employ the actual soil-point averages and to express these and the irrigator averages in terms of milligrams. Thus the final soil-point average previously given (0.61 gm.) becomes 9.9 mgm./12 sq. cm. (or 0.83 mgm./sq. cm.), and the final irrigator average (0.62 gm.) becomes 620 mgm./100 sq. cm. (or 6.2 mgm./sq. cm.).

Averages for the several mixtures

When the five primary soil-point averages for each soil mixture are averaged, the resulting values (which are listed in the serial order of the mixtures, from 1 to 16) are as follows: 8.3, 7.5, 9.7, 8.9, 11.2, 7.7, 11.8, 11.2, 6.6, 10.8, 6.3, 8.8, 9.9, 13.9, 11.7, 12.1 mgm./12 sq. cm. These values multiplied by

62 are the ones represented by the ordinates of the horizontal bars shown in the lower part of figure 3 and by the ordinates of the points of record on the continuous-line graph in the lower part of figure 2. Their magnitude range is only from 6.3 mgm. to 13.9 mgm., the grand average for all soils and all tests being 9.9 mgm., as has been noted. Although this index apparently varied in a minor and not readily understandable way with soil composition (see fig. 4, A), it shows no consistent variation with respect to water-holding power and its variation was so slight as to be of doubtful significance when water-supplying power is considered with reference to the welfare of ordinary plants. Expressed with reference to unit area, these sixteen values become: 0.69, 0.63, 0.81, 0.74, 0.93, 0.64, 0.98, 0.93, 0.55, 0.90, 0.53, 0.73, 0.83, 1.16, 0.98, 1.01 mgm./sq. cm., and their average is 0.83 mgm./sq. cm.

When the five primary irrigator averages for each soil mixture are averaged the resulting values, listed in the serial order of the mixtures, are as follows: 0.36, 0.70, 1.76, 1.72, 0.80, 0.69, 2.67, 0.58, 0.61, 0.73, 0.79, 0.61, 0.44, 0.75, 0.65, 0.50 ml./100 sq. cm. These values are the ones represented by the ordinates of the bars shown in the upper part of figure 3 and by the ordinates of the points of record on the broken-line graph in the lower part of figure 2. When the three exceptionally high values (for mixtures 3, 4 and 7) are omitted, the magnitude range of the remaining thirteen is from 0.36 ml. to 0.80 ml. and the grand average for all thirteen soils and all tests is 0.62 ml./100 sq. cm. It is remarkable that the breadth of range is relatively almost exactly the same for these thirteen irrigator values as for all the soil-point values; on the basis of the lower limit in each case, the two ranges are from unity to 2.222 (irrigator) and from unity to 2.206 (soil-point cone). The irrigator values just given may be expressed in terms of milligrams per square centimeter of surface simply by dividing each by 10; thus 0.36 ml./100 sq. cm. (essentially 0.36 gm./100 sq. cm.) is equivalent to 3.6 mgm./sq. cm.

Initial water-supplying power of the soil adjacent to plant roots at beginning of permanent wilting

The nearly uniform 5–7-cm. soil-point values of our soil mixtures at the times of our soil tests (when the plants had been permanently wilted for 12 hours or more) were markedly lower than the critical values reported for coleus and wheat by Livingston and Koketsu (19) and for coleus by Wilson and Livingston (37). Both of those studies were carried out in the same greenhouse as was used for the study now reported. Livingston and Koketsu employed a 2-hour period of exposure, and their porcelain soil points were slightly different from those used by later students and by ourselves. With a series of soil mixtures much like ours, they found that potted plants of coleus and wheat passed into permanent wilting when the initial water-supplying power of the soil had decreased to about 8.5 mgm./sq. cm./2 hr. For the first hour this value may perhaps be estimated as about 4.5 mgm./sq. cm., or 54 mgm./12 sq. cm./hr. Wilson and Livingston's potted coleus plants, grown in soil somewhat lighter than the moist sand of our soil mixtures,

showed incipient drought effects when the initial 5–7-cm. soil-point reading was about 100 mgm./12 sq. cm.; they began to wilt when that reading was 40 mgm./12 sq. cm. and they were badly wilted when it had decreased to 36 mgm./12 sq. cm. These plants had passed far beyond the beginning of permanent wilting ("leaves dried up") when the reading had decreased to 29 mgm./12 sq. cm. Perhaps the initial water-supplying power of the soil actually adjacent to the roots of their coleus plants at the onset of permanent wilting may be estimated as about 40 mgm./12 sq. cm., or about 3.3 mgm./sq. cm./hr. With the exception of two species of Festuca, their plants in flats had already passed the beginning of permanent wilting when the 5–7-cm. reading still remained above 30 mgm./12 sq. cm.

On the other hand, at the times of our own tests (12 or more hours after permanent wilting had presumably set in) our initial 5–7-cm. soil-point reading was only about 9.9 mgm./12 sq. cm. (0.83 mgm./sq. cm.), thus much smaller than the estimates just mentioned. This difference is perhaps not surprising when it is remembered that the surface soil of such pot cultures generally dries rapidly after it has ceased to be obviously wet, that our pots were deeper than those of Livingston and Koketsu and of Wilson and Livingston, that our empty irrigators surely retarded upward movement of water from the region of root absorption to the region of evaporation, and that our soil tests were delayed considerably after the onset of permanent wilting.

For healthy growth of ordinary potted plants, a gardener generally applies water to his pots frequently enough to maintain an initial 5–7-cm. soil-point reading above 500–1000 mgm./12 sq. cm./hr. Shortly after each watering of our pots this value was 2,000 mgm. or greater. This is always true for the standard Livingston soil-point cone when applied superficially to recently watered soils of whatever kind. For potted plants of the mesophyte type, health is not apt to be impaired on account of soil-moisture deficiency until this reading falls below 150 or 100 mgm./12 sq. cm./hr. Oxygen supply to the roots may become inadequate for some plants, however, when the initial 5–7-cm. reading remains above 1,500 or 2,000 mgm. for sufficiently long periods. For most shallow-rooted mesophytes, it appears that the range of the initial 5–7-cm. soil-point reading within which health is likely to be maintained—as far as soil moisture and soil oxygen are concerned—may perhaps be safely estimated as from about 100 or 150 mgm. to about 1,000 or 1,200 mgm./12 sq. cm./hr.

Our critical soil-point average of 9.9 mgm./12 sq. cm. for all soil mixtures (with range from 6.3 to 13.9 mgm.) may be compared also with the corresponding values obtained by Marshall (22) for conifer seedlings grown in flats of sand in this same greenhouse. In his experiments the instruments employed and the technique of their use were essentially the same as in the studies of Wilson and Livingston and of ourselves, but his method for fixing upon his critical stage of wilting was perhaps much more satisfactory than any thus far employed by any other experimenter in this field; he used the average water content of seedling tops as his criterion of the progress of wilt-

ing. His soil masses had about the same depth as those of Wilson and Livingston. His critical soil-point values (for soil depth of 3–5 cm. rather than 5–7 cm.), for seedlings that had been watered in the usual way throughout their growth period before drought began, ranged from 11 mgm./12 sq. cm. (25-day-old seedlings of western yellow pine) to 26 mgm./12 sq. cm. (Norway spruce seedlings of that same age). The highest individual soil-point reading obtained by us was 23 mgm./12 sq. cm./hr.

Mason (23), whose paper includes a very useful discussion of the general concept of water-supplying power of the soil, studied the onset of permanent wilting in pot-grown maize plants, using wooden soil-point cones (lead pencils) and an application period of 3 hours. Hardy (7, 8) studied field soils in Trinidad by a similar method, with reference to the growth of sugar cane. Follet-Smith (4) also studied the water-supplying power of the soil of sugar-cane plots in Trinidad, using porous-porcelain soil points and an application period of 3 hours or less. With cane plants much injured by drought, the water-supplying power of the soil about their roots was found to be about 1.8 mgm./sq. cm./hr. From the data of Mason and Hardy he calculated that the critical supplying-power value at the beginning of permanent wilting was about 2.1 mgm./sq. cm./hr. (25.2 mgm./12 sq. cm./hr.) for maize and about 2.6 mgm./sq. cm./hr. (31.2 mgm./12 sq. cm./hr.) for sugar cane.

Livingston and Ohga (20) reported that grasses of the lawns of the Johns Hopkins University grounds had lost much of their green color on account of natural drought when standard soil points (like those of the present study and applied in the same way) gave initial readings of about 12 mgm./12 sq. cm./hr. at the 5–7-cm. depth. These grasses were completely brown when the soil-point readings were about 5 mgm. Finally, Wilson's (36) 5–7-cm. soil-point values for this same lawn were less than 20 mgm./12 sq. cm./hr. only when the grass leaves were dead or rapidly dying.

In a general way we may say that the water-supplying power of the soil adjacent to absorbing roots at the onset of permanent wilting appears to vary considerably with the kinds of plants considered and with their physiological condition, probably sometimes also with weather conditions at the time of wilting, but that it appears to be almost or quite independent of the kind of soil employed. As to the range of this critical value, it is perhaps safe to add that it may generally be well above 24 and below 60 mgm./12 sq. cm./hr. (i.e., between about 2 and 5 mgm./sq. cm./hr.). For pot-grown coleus in our greenhouse we think our average (9.9 mgm./12 sq. cm./hr.) is much lower than the critical value, which may be tentatively estimated as about 40 mgm./12 sq. cm./hr. (i.e., about 3.3 mgm./sq. cm./hr.—perhaps between 2.8 and 3.8 mgm./sq. cm./hr.).

Initial water-absorbing power of soil adjacent to plant roots at beginning of permanent wilting

Since the present study is the first attempt to measure the water-absorbing power of the soil, there are no data available from other studies, with which

to compare our irrigator values. It may be supposed however, for reasons already mentioned, that the average irrigator value for thirteen of our soil mixtures represents the absorbing power of these mixtures in the vicinity of the plant roots at the times of test. However, because this value is probably somewhat too large to represent the soil adjacent to the roots when permanent wilting had just set in—since our readings were delayed—the critical irrigator reading for the onset of permanent wilting may be estimated as perhaps somewhere between 500 and 600 mgm./100 sq. cm./hr., instead of 620 mgm., which is our average. This smaller value (which may be stated as between 5 and 6 mgm./sq. cm./hr.) may be tentatively taken to correspond approxi-

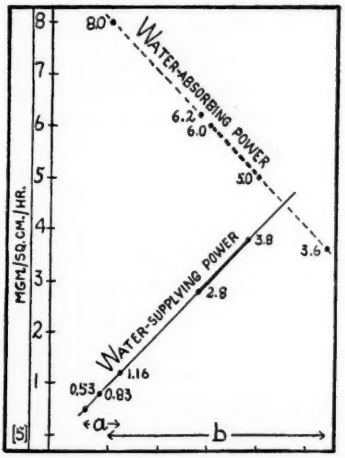

FIG. 5. HYPOTHETICAL SCHEME TO SHOW GENERAL RELATIONS OF WATER-SUPPLYING POWER AND WATER-ABSORBING POWER FOR LOW VALUES OF THE FORMER AND HIGH VALUES OF THE LATTER

Lengths of two-headed arrows indicate: (*a*) range of 5–7-cm. supplying power in the present study, (*b*) range of 9–15-cm. absorbing power in the present study. Broad lines represent estimated probable range of critical supplying power and absorbing power at onset of permanent wilting of greenhouse-grown coleus.

mately to our estimate of the corresponding critical soil-point reading for coleus—somewhere between 2.8 and 3.8 mgm./sq. cm./hr.

General relations between water-supplying power and water-absorbing power of soils

For a given soil mass, water-supplying power at a given depth increases, of course, with increasing water content, until the supplying power becomes very great when field saturation is approached; and water-absorbing power decreases correspondingly, until it vanishes. The general relations between supplying power and absorbing power are set forth by the hypothetical diagram of figure 5, where our data for the three exceptional soil mixtures are

disregarded and it is tentatively assumed that absorbing power generally varies inversely as supplying power within the range considered.

On the diagram, abscissas represent initial water-supplying power of the soil adjacent to the instrument, expressed as milligrams per square centimeter, for the first hour of test. The graph for soil-point values (continuous line) is rectilinear and slopes upward to the right, at an angle of 45°—on the reasonable supposition that these values are essentially actual indices of the supplying power of the adjacent soil. Consequently the two coördinates of any point of that graph are always equal. Points are marked for the supplying-power values 0.53 and 1.16 mgm./sq. cm./hr. (the limits of the range of our experimental averages) and for 0.83 mgm./sq. cm./hr. (our grand average for all soil mixtures and all tests). The region for values from 2.8 to 3.8 mgm./sq. cm./hr. is marked as a broad line, to represent the range within which, as we have estimated, the critical initial supplying power for the beginning of permanent wilting may be supposed to lie.

The graph for irrigator values (broken line) is also rectilinear, and it is arbitrarily drawn perpendicular to the other; its angle and curvature may be incorrect. On this graph are marked points for 3.6 and 8.0 mgm./sq. cm./hr. (the limits of our irrigator range) and also for 6.2 mgm./sq. cm./hr. (our grand irrigator average for thirteen soils). The region for values from 5 to 6 mgm./sq. cm./hr. is marked as a broad line, to represent the range within which the critical absorbing power for the onset of permanent wilting may be supposed to lie. On this diagram the two graphs cross at a point representing the soil condition for which both instruments should give the same value, but the coördinates of that point may be incorrect. Two-headed horizontal arrows indicate (*a*) our range of soil-point values for the 5–7-cm. depth and (*b*) our range of irrigator values for the 9–15-cm. depth. These two kinds of readings refer to quite different sets of soil-moisture conditions; for the soil layer tested by means of soil-point cones was always much drier than that tested by means of irrigators in the same pot, the irrigator cones being more deeply situated, in the region of root absorption.

We think this partially hypothetical diagram may be qualitatively correct, although the quantitative relations shown by it will surely require modification if and when additional experimental data on this general question become available. At any rate, the diagram may offer a point of departure for further experimentation concerning water-supplying power and water-absorbing power and their relations to each other and to plant performance under otherwise favorable conditions for health.

SUMMARY AND CONCLUSION

The general relations brought out by this study of advanced wilting in greenhouse pot cultures of coleus and wheat lend further support to the still commonly neglected proposition that soil-moisture conditions, when considered in relation to the performance of plants with roots in soil, call for an

approach from the dynamic viewpoint, involving the concepts of water-supplying and water-absorbing power of the soil.

Our numerical results with soil-point cones furnish additional support to the conclusion that that instrument promises to be exceedingly useful whenever the dynamic water relations between plant and soil are to receive attention. It is again emphasized that ordinary plants respond, in their subterranean water relations, directly to the water-supplying power of the soil adjacent to their absorbing roots, rather than to soil suction or to soil-moisture content referred to moisture equivalent, water-holding capacity, hygroscopic coefficient, or other such static soil characteristics that represent internal soil surface, etc. Of course these static characteristics of a soil determine its water-supplying power at any specified temperature, but supplying power is the environmental feature that directly limits the rate of water absorption and it may be measured and studied quantitatively for the purposes of physiology without reference to the static characteristics of the soils considered.

The attainment by a drought-affected plant to a critical stage of wilting, such as the onset of permanent wilting, is again shown as corresponding to a critical water-supplying-power value of the soil about the roots—a value that is essentially the same for soils of greatly different static properties. When the coleus and wheat plants of these experiments were all in essentially the same advanced stage of wilting, the water-supplying power at the 5–7-cm. depth was essentially the same for the sixteen different soil mixtures studied, whether the soil was light or heavy, whether its volumetric water-holding capacity was below 50 per cent or above 90 per cent.

Some evidence was found, however, to support the proposition that soil composition with reference to loam, humus, and sand content, which is a static soil feature, may in some instances exert a very minor influence on the critical water-supplying-power value that corresponds to a critical advanced stage of plant wilting. That proposition is not yet well established and it calls for further study.

A new device for quantitatively estimating the water-absorbing power of a soil mass at any desired depth and from time to time, without disturbing the soil after the instrument is installed, proved highly promising. A Livingston porous-porcelain irrigator cone remains permanently in the soil, at any specified depth. It is temporarily filled with water for a short time while each reading is being made, but it remains empty at other times. Readings of the rate of water loss for 1 hour are obtained by means of a burette, a mercury barostat being introduced between burette and cone. For the critical stage of wilting considered, there was generally a constant proportionality between water-absorbing-power readings of the irrigator device at the 9–15-cm. depth and corresponding water-supplying-power readings of soil-point cones at the 5–7-cm. depth. But three exceptional soil mixtures gave markedly excessive irrigator readings, although the corresponding soil-point

readings of these mixtures were not unusual. The question concerning these three exceptional soil-mixtures calls for further study.

By means of permanently placed instruments of this or of similar type, it should be feasible to follow the fluctuations in the moisture condition of a field soil at any depth desired, without recourse to any special study of soil-moisture contents. The new device measures a dynamic soil feature that is related to water-supplying power. It is not limited in its utility range, as are the tonometers thus far described for estimating soil suction, and it is easily and cheaply constructed and installed. Details concerning its performance require further attention, and it is likely to be improved. It gave results somewhat less precise than those given by soil-point cones (by which water-supplying power is measured), but its measurements are volumetric, whereas those of soil-point cones are gravimetric and the latter instruments cannot be applied without disturbing the soil to some extent at each test.

As any moist soil mass dries out, its water-supplying power decreases and its water-absorbing power increases, and these changes naturally occur most rapidly in the immediate vicinity of plant roots and near the free soil surface. Critical values of these dynamic powers should naturally refer to the soil layer in the immediate vicinity of the absorbing roots. Some attention is given to the general relations that appear to obtain between water-supplying power and water-absorbing power and between them and the onset of permanent wilting in plants.

REFERENCES

(1) ALWAY, F. J. 1913 Studies of the relation of the non-available water of the soil to the hygroscopic coefficient. *Nebr. Agr. Exp. Sta. Res. Bul.* 3: 5–122.

(2) BRIGGS, L. J., AND SHANTZ, H. L. 1912 The wilting coefficient for different plants and its direct determination. U. S. Dept. Agr. Bur. Plant Indus. Bul. 285.

(3) CALDWELL, J. S. 1913 The relation of environmental conditions to the phenomenon of permanent wilting in plants. *Physiol. Res.* 1: 1–56.

(4) FOLLET-SMITH, R. R. 1929 The water-supplying power of certain Trinidad sugar-cane soils. *Min. and Proc. Froghopper Invest. Com.* 2 (part 15): 188–216.

(5) GARDNER, W., ISRAELSEN, O. W., EDLEFSEN, N. E., AND CLYDE, H. S. 1922 The capillary potential function and its relation to irrigation practice. *Phys. Rev.* 20: 196.

(6) HAINES, W. B. 1930 Studies in the physical properties of soils. V. The hysteresis effect in capillary propefties and the modes of moisture distribution associated therewith. *Jour. Agr. Sci.* 20: 97–116.

(7) HARDY, F. 1923 The soil-point method for directly estimating the water-supplying power of a soil in the field. *Jour. Agr. Sci.* 13: 357–360.

(8) HARDY, F. 1924 Field measurement of soil moisture. *Trop. Agr.* [Trinidad] 1: 98–100.

(9) HILGARD, E. W. 1912 Soils. New York.

(10) KELLY, A. P. 1927 The suction force of soils and its demonstration in the plant habitat. *Proc. First Internatl. Cong. Soil Sci.* 1: 535–538.

(11) KORNEV, V. G. 1924 The suction force of soils. *Zhur. Opytn. Agron.* [Russian] 22: 105–111 (1921–23). Abs. *Soil Sci.* 17: 428 (1924).

(11a) KRAMER, PAUL J. 1937 The relation between rate of transpiration and rate of absorption of water in plants. *Amer. Jour. Bot.* 24: 10–15.

(12) LIVINGSTON, B. E. 1906 The relation of desert plants to soil moisture and to evaporation. *Carnegie Inst. Wash. Pub.* 50.

(13) LIVINGSTON, B. E. 1918 Porous clay cones for auto-irrigation of potted plants. *Plant World* 21: 202–208.

(14) LIVINGSTON, B. E. 1917 Incipient drying and temporary and permanent wilting of plants, as related to external and internal conditions. *Johns Hopkins Univ. Cir.* 293: 133–153.

(15) LIVINGSTON, B. E. 1934 Possible Importance of respiration water to young wheat seedlings. *Bul. Torrey Bot. Club* 61: 217–223.

(16) LIVINGSTON, B. E., AND HAASIS, FERDINAND W. 1929 The measurement of evaporation in freezing weather. *Jour. Ecology* 17: 315–328.

(17) LIVINGSTON, B. E., AND HAWKINS, LON A. 1915 The water relation between plant and soil. *Carnegie Inst. Wash. Pub.* 204: 1–42.

(18) LIVINGSTON, B. E, HEMMI, TAKEWO, AND WILSON, J. D. 1926 Growth of young wheat plants in auto-irrigated soils as related to the water-supplying power of the soil and to the adjustment of the auto-irrigator. *Plant Physiol.* 1: 387–395.

(19) LIVINGSTON, B. E., AND KOKETSU, RIICHIRO 1920 The water-supplying power of the soil as related to wilting of plants. *Soil Sci.* 9: 467–485.

(20) LIVINGSTON, B. E., AND OHGA, ICHIRO 1926 The summer march of soil conditions on a lawn. *Ecology* 7: 427–439.

(21) LYNDE, C. J., AND DUPRE, H. A. 1913 On a new method of measuring the capillary lift of soils. *Jour. Amer. Soc. Agron.* 5: 107–116.

(22) MARSHALL, ROBERT 1931 An experimental study of the water relations of seedling conifers with special reference to wilting. *Ecolog. Monog.* 1: 39–98.

(23) MASON, T. G. 1922 The physiological humidity of the soil and its direct determination. *West Indian Bul.* 19: 137–154.

(24) PULLING, HOWARD E. 1917 The rate of water movement in aerated soils. *Soil Sci.* 4: 239–268.

(25) PULLING, HOWARD E., AND LIVINGSTON, B. E. 1915 The water-supplying power of the soil as indicated by osmometers. *Carnegie Inst. Wash. Pub.* 204: 49–84.

(26) RICHARDS, L. A. 1928 The usefulness of capillary potential to soil moisture and plant investigators. *Jour. Agr. Res.* 37: 719.

(27) RICHARDS, L. A., AND GARDNER, WILLARD. 1936 Tensiometers for measuring the capillary tension of soil water. *Jour. Amer. Soc. Agron.* 28: 352–358.

(28) ROGERS, W. S. 1935 A soil moisture meter depending on the "capillary pull" of the soil, with illustrations of its use in fallow land, grass orchard, and irrigated orchards. *Jour. Agr. Sci.* 25: 326–343.

(29) ROGERS, W. S. 1935 Root studies. VI. Apple roots under irrigated conditions, with notes on the use of a soil moisture meter. *Jour. Pomol. and Hort. Sci.* 13: 190–201.

(30) ROGERS, W. S. 1936 The relation of soil moisture to plant growth, illustrated by moisture meter experiments with strawberries. *Ann. Rpt. East Malling Res. Sta.* 1935: 111–120.

(31) SCHOFIELD, R. K. 1935 The pF of the water in soil. *Trans. Third Internatl. Cong. Soil Sci.* 2: 37–48.

(32) SHIVE, J. W., AND LIVINGSTON, B. E. 1914 The relation of atmospheric evaporating power to soil moisture content at permanent wilting in plants. *Plant World* 17: 81–121.

(33) VEIHMEYER, FRANK J. 1927 Some factors affecting the irrigation requirements of deciduous orchards. *Hilgardia* 2: 125–284.

(34) VEIHMEYER, FRANK J., AND HENDRICKSON, A. H. 1927 Soil moisture conditions in relation to plant growth. *Plant Physiol.* 2: 71–82.

(35) WHITNEY, M., AND CAMERON, F. K. 1903 The chemistry of the soil as related to crop production. U. S. Dept. Agr. Bur. Soils Bul. 22.

(36) WILSON, J. DEAN 1927 The measurement and interpretation of the water-supplying power of the soil with special reference to lawn grasses and some other plants. *Plant Physiol.* 2: 385–440.

(37) WILSON, J. DEAN, AND LIVINGSTON, B. E. 1932 Wilting and withering of grasses in greenhouse cultures as related to water-supplying power of the soil. *Plant Physiol.* 7: 1–34.

ELECTRODIALYSIS AND CATION EXCHANGE STUDIES ON SOILS OF VARYING ORGANIC MATTER CONTENT[1]

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In a previous paper (15) the authors made a study of the effect of phosphates on the cation exchange capacity of certain soils that had been under treatment with different amounts of phosphates at the New Jersey Agricultural Experiment Station. It is well known from the work of McGeorge (7), Tiulin (16), and Waksman (18) that the organic matter content of soil also has an important influence on the cation and anion exchange capacity of soils. In other words, the "humates" appearing in the colloidal organic fraction of the soil, as well as the phosphates and silicates from the inorganic fraction, as pointed out by Mattson (9), act as acidoids.

Numerous papers appearing in the literature (6, 7, 18, 19) deal with the isolation and identification of fractions of the so-called "humus material." These papers have been well summarized by Waksman in his recent book on humus (18). At present the cation exchange capacity of humus has been attributed to several groups of complexes; namely, ligno-humate (7, 19) and ligno-proteins, and combinations of these with metallic cations. It has also been pointed out by Muller (13) that the degree of decomposition of the organic matter affects its cation exchange capacity. Sugars and hemicelluloses are destroyed during decomposition, leaving a residue relatively high in the ligno-humate fraction (18). It is probably because of this relative increase in the ligno-humate fraction that the decomposed material has a greater ability to retain bases than has the original undecomposed material.

Certain plots on the nitrogen availability series at the New Jersey Agricultural Experiment Station, which have been under treatment for nearly 30 years, offered excellent material for this investigation. The plots chosen for study were examined in the light of the newer knowledge of the physical chemistry of soils. The soil type is Sassafras loam. The data at top of page 206 indicate the fertilizer treatment on the acre basis for four unlimed and four limed plots designated "A" and "B" respectively.

In the earlier part of the work superphosphate and muriate of potash were used in twice the amount now used. For the limed section, lime in the carbonate form has been used at the rate of 2 tons to the acre at 5-year intervals,

[1] Journal Series paper of the New Jersey Agricultural Experiment Station, department of soil chemistry and bacteriology.

Plot	*Special Treatment*
7A, 7B	Nothing
5A, 5B	Minerals* and 16 tons cow manure† an acre
18A, 18B	Minerals, 16 tons cow manure‡, and 320 pounds nitrate of soda
19A, 19B	Minerals only

* Minerals = 320 pounds superphosphate and 160 pounds nitrate of soda
† Since 1933, 4 tons of dehydrated cow manure.
‡ Since 1933, 2 tons of dehydrated cow manure.

with the exception that none has been applied since 1928, the soil reaction being maintained between 6.0 and 7.0.

METHODS

Electrodialysis of the soil samples was conducted with a Mattson cell (8). One hundred gram samples were placed in the center compartment, and approximately 200 cc. of distilled water was added. In the cathode and anode chambers about 400 cc. of distilled water was added. In the former the electrode consisted of copper gauze, whereas in the latter the electrode was platinum. A direct current of approximately 100 milliamperes was maintained during the period of dialysis, the current being furnished by a mercury tube rectifying unit. To prevent heating, a glass cooling unit was inserted in the soil compartment and a constant flow of cold tap water was maintained through it during electrodialysis. At different time intervals the cathode and anode liquors were tapped off and set aside for titration, the chamber being refilled with distilled water. Electrodialysis was considered to be complete when not more than 0.1 m.e. of titrable bases was delivered in 8 hours.

The dialyzable bases and acids were titrated with 0.2 *N* sodium hydroxide and 0.2 *N* nitric acid respectively, phenolphthalein being used as the indicator.

The total cation exchange capacity and the exchangeable hydrogen were determined by the normal barium acetate method outlined in a previous paper (15).

Determinations of pH were made with a Leeds and Northrup glass electrode on a 1:1 soil suspension.

Ultimate pH determinations were made on the electrodialyzed sample which had been first dried at a temperature of 60–65°C. and then exposed to the moisture of the air.

Carbon determinations were run on the original soil by the method of Tiurin (17).

Analysis of dialyzates:

a. Silica was determined in these solutions in the usual manner except in the anode liquor where organic matter appeared. In such cases the organic matter was removed with hydrogen peroxide before the silica was stabilized.

b. Iron was determined in an aliquot by the usual sulfocyanate colorimetric method after the removal of silica.

c. Phosphorus was determined in an aliquot of the anode liquor by the usual precipitation with ammonium molybdate and subsequent titration of the precipitate after removal of silica.

Analysis of the sediment appearing in the cathode liquor from the cylinder soils: Carbon in the sediment was determined by the electric combustion method and loss on ignition was determined in the usual manner. The ash was fused with sodium carbonate, and the resulting melt was analyzed for silica, the sesquioxides, manganese, calcium, and magnesium.

DISCUSSION OF RESULTS

In table 1 data on the total dialyzable bases and acids and the amounts dialyzable at various intervals are presented and compared with the pH of the field sample. It is apparent that there is no correlation between the total bases delivered and the field pH. For example, the pH values on the limed plots are nearly the same (close to 6.5) and yet the total bases vary from 3.2 m.e. to 6.7 m.e. This is in line with the findings of Pierre and Scarseth (14). It is also to be noted that liming has increased the total titrable bases. This increase is reflected in the degree of unsaturation of the soils. Thus, in table 2 it can be seen that the percentage of unsaturation is much less on the limed plots than on the unlimed plots in each case. On the unlimed plots with manure and minerals the percentage of unsaturation is less than that on the plots receiving minerals alone or nothing. Thus on plots 5A and 18A the percentage of unsaturation was 38.6 and 32.1 per cent respectively, whereas on 7A and 19A it was 74.9 and 47.6 per cent. This is no doubt due to the fact that the organic matter plots are richer in bases which were contained in the large amounts of manure added.

It is of further interest to note from table 1 that the bulk of the bases are released in the first 14 hours. In fact, between 70 and 80 per cent of the total dialyzable bases are liberated in the first 6 hours. Mattson and Loddesel (5, 11) have previously reported similar results. In most of the limed plots electrodialysis had to be continued for 38 hours to release the bases completely. When the base saturation of the soil reached a certain point (pH 5.4) (11) sediment appeared in the cathode dialyzates. With the exception of the untreated plots, this occurred in the 6–14-hour period of electrodialysis. The quantity of sediment decreased, however, with increasing time intervals until at the 30–38-hour interval the cathode solution was only faintly turbid. This phenomenon has been well elucidated by Mattson (11). He has shown that the appearance of the sediment in the cathode chamber is due to the fact that complex electropositive ions of iron, aluminum, silica, and humus migrate to the cathode chamber through the membrane and precipitate here, because the pH in the cathode chamber is higher than the isoelectric pH of the ionized complexes. In this connection Mattson (11) states: "The precipitation of the ions at the membrane builds up a new complex which is richer in sesquioxides and poorer in silica (and humus) than the original soil complex. Its ultimate

pH and isoelectric point are therefore higher and will finally reach a value at which no ions of Al and Fe will be able to penetrate the layer, not even after complete unsaturation. No sediment will then appear in the cathode solution but basic material will continue to be ionized within the more acid soil mass and be transported toward the cathode membrane where the amphoteric ions will lose their charge and be precipitated."

The titrable acids are also recorded in table 1. The total quantity of acids titrated represents the sum of the organic and mineral acids. Here, as in the case of the bases, the total acids delivered are greater on the limed than on the unlimed series. On soil from the organic matter plots the anode dialyzates were intense yellow in color, and upon concentration organic matter appeared. This is in line with the observations of Anderson and Byers (1). The higher quantity of titrable acids on the limed plots must be attributed in part to larger amounts of dialyzable phosphates from these plots (table 3). It is also possible that because of greater decomposition of the organic matter on the limed plots more organic acids were produced.

The rate at which the acids were delivered during electrodialysis was very similar to that of the bases. In other words, the bulk of the titrable acids came out in 14 hours, with most of them appearing in the first 6 hours.

Ultimate pH determinations of the electrodialyzed soils from the plots are recorded in table 2. It should be pointed out that two main factors influence the ultimate pH value of colloidal material: first, the ratio of combined acidoids to combined basoids as determined by the chemical composition of the material (2) (free SiO_2, Fe_2O_3, and Al_2O_3 should not be considered in determining this ratio); secondly, the nature of the acidic material, i.e., whether the acidoids are humates, phosphates, or silicates. From table 2 it can be seen that in general the ultimate pH values are lower than the field pH. Plot 7A, however, is the exception. As pointed out by Mattson (12), in this case the original soil contained diffusible acids which were removed during the process of electrodialysis and hence brought about a higher ultimate pH. The ultimate pH values on the plots receiving manure and minerals (5A and 18A), or manure, minerals, and lime (5B and 18B) show a decrease of approximately 0.4 to 0.6 pH unit when compared to plots receiving nothing (7A), minerals (19A), or minerals and lime (19B). This undoubtedly is because with these plots the acidoid-basoid ratio has been increased by the addition of organic matter and phosphorus. It can be seen in table 2 that soil from the organic matter plots average about 0.8 per cent higher in carbon than the plots receiving no organic matter.

The data on the cation exchange capacity before and after electrodialysis are also presented in table 2. Soil from the organic matter plots shows a much higher cation exchange capacity both before and after electrodialysis than does soil from the plots receiving no organic matter. This might be expected from the ultimate pH values already discussed. Thus as the soil colloidal complex becomes more acidic in nature the cation exchange capacity

TABLE 1

Electrodialyzable bases and acids in soils from field plots

Sassafras loam

PLOT	TREATMENT	FIELD pH	TOTAL BASES†	BASES IN DIALYZATE FRACTIONS				TOTAL ACIDS†	ACIDS IN DIALYZATE FRACTIONS			
				0–6 hr.	6–14 hr.	14–30 hr.	30–38 hr.		0–6 hr.	6–14 hr.	14–30 hr.	30–38 hr.
			m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*
7A	Nothing	4.53	0.202	0.202‡	0.000	.....	.....	0.341	0.160	0.181	.....	.....
7B	Lime only	6.50	3.345	2.201	0.522‡	0.522‡	0.100‡	0.863	0.382	0.181	0.160	0.140
5A	16 tons manure and minerals*	5.56	3.577	2.935	0.542‡	0.100‡	.....	2.217	1.186	0.408	0.623	.....
5B	16 tons manure, lime, and minerals	6.50	4.824	3.658	0.945‡	0.161‡	0.060	2.572	1.266	0.583	0.583	0.140
18A	16 tons manure, minerals, and 320 pounds $NaNO_3$	5.71	3.437	2.633	0.703‡	0.101‡	.....	2.010	0.864	0.543	0.603	.....
18B	16 tons manure, lime, minerals, and 320 pounds $NaNO_3$	6.52	6.692	4.602	1.849‡	0.201‡	0.040‡	2.310	1.266	0.342	0.523	0.181
19A	Minerals	4.86	0.442	0.442	0.000‡	.....	.....	0.261	0.020	0.241	.....	.....
19B	Minerals and lime	6.37	3.155	2.492	0.623‡	0.040‡	.....	1.447	0.763	0.342	0.342	.....

* P, K.

† m.e. per 100 gm.

‡ Sediment.

also increases. On soil from the plot receiving minerals only, the cation exchange capacity has also been increased over that from the plot receiving nothing. This would be expected, since the addition of phosphorus has increased the acidoid-basoid ratio.

Electrodialysis of the soil material has reduced the cation exchange capacity in all cases. The loss in this property is higher on the limed soil than on the unlimed. The greatest losses, however, are to be noted on the plots receiving lime and manure. Thus plots 5B and 18B showed a loss of 2.8 and 3.04 m.e.

TABLE 2

Data on field plots with various treatments

Sassafras loam

PLOT	TREATMENT	FIELD pH	ULTIMATE pH	CARBON CONTENT OF SOIL†	EXCHANGEABLE HYDROGEN PER 100 GM. SOIL BY BARIUM ACETATE	UNSATURATION	CATION EXCHANGE CAPACITY PER 100 GM. SOIL BY BARIUM ACETATE		
							Before electrodialysis	After electrodialysis	Difference
				per cent	*m.e.*	*per cent*	*m.e.*	*m.e.*	*m.e.*
7 A	Nothing	4.53	4.69	0.90	3.98	74.9	5.31	4.72	0.59
7 B	Lime	6.43	4.42	1.11	1.17	18.4	6.35	5.11	1.24
5 A	16 tons manure and minerals*	5.56	4.21	1.89	4.35	38.6	11.26	10.18	1.08
5 B	16 tons manure, lime, and minerals	6.50	4.04	1.64	1.78	17.5	10.15	7.35	2.80
18 A	16 tons manure, minerals, and 320 pounds $NaNO_3$	5.71	4.04	1.83	3.49	32.1	10.87	8.98	1.89
18 B	16 tons manure, lime, minerals, and 320 pounds $NaNO_3$	6.52	4.13	1.84	1.56	13.6	11.43	8.39	3.04
19 A	Minerals	4.86	4.48	1.13	3.67	47.6	7.71	6.87	0.94
19 B	Minerals and lime	6.37	4.41	0.98	1.41	16.2	8.68	6.31	2.37

* P, K.

† Before electrodialysis.

respectively as against 1.08 and 1.89 m.e. on the unlimed plots. This reduction in cation exchange capacity of the electrodialyzed samples is due to two factors: first, the removal of hydrolyzed acidoids, and secondly, the precipitation on the parchment paper and in the cathode chamber of complexes which show cation exchange power.

In table 3 is given the P_2O_5 content of the anode liquor from the various plots. It is apparent that the limed plots show a higher P_2O_5 content than do the unlimed plots. This may no doubt be explained on the assumption that when phosphorus was applied to these limed plots calcium phosphate, rather

than iron and aluminum, complexes were formed largely. Probably the reverse was true on the unlimed plots. These calcium phosphate complexes formed are easily hydrolyzed during the process of electrodialysis and hence yield a greater quantity of P_2O_5. Both the manured plots limed and unlimed were higher in P_2O_5 content than the untreated plot or the plot receiving minerals only. Here, of course, the higher phosphorus content might be due to the added phosphorus in the manure or to a displacement of phosphorus by the humate fraction.[2]

In table 3 are given also the amounts of SiO_2 from the anode and the cathode chambers. The silica appearing in the anode liquors represents the sum of the hydrolyzable silicates and silica which may have moved in conjunction with iron and aluminum as a complex electronegative micelle. The limed plots yielded more silica both in the anode and in the cathode solutions than

TABLE 3

The removal of ionized acidoids and of acidoids from ionogens from certain field soils during electrodialysis

PLOT	P_2O_5 IN ANODE CHAMBER	SiO_2 IN ANODE CHAMBER	SiO_2 IN CATHODE CHAMBER	TOTAL ACIDOIDS* REMOVED DURING ELECTRODIALYSIS
	m.e.	*m.e.*	*m.e.*	*m.e.*
7 A	Trace	0.164	0.264	0.428
7 B	0.130	0.412	0.364	0.906
5 A	0.770	0.364	0.260	1.394
5 B	0.825	0.500	0.584	1.909
18 A	0.650	0.452	0.264	1.366
18 B	0.845	0.584	0.404	1.833
19 A	0.130	0.144	0.164	0.438
19 B	0.505	0.364	0.244	1.113

* Considerable quantities of organic matter moved to the anode chamber during electrodialysis. Values recorded in the above table represent the sum of the mineral acidoids electrodialyzed.

did the unlimed plots, since the complexes on the limed plots had a lower ultimate pH. As was expected, considerable quantities of organic matter moved to the anode during electrodialysis (as indicated by the color of the liquor), the amount being the greatest from the manured plots.

It can be seen in the last column of table 3 that the total quantities of acidoids hydrolyzed are greater on the limed than on the unlimed plots and still greater on the plots receiving manure.

Another point of interest is brought out by the data in table 4. Iron determinations on the dialyzates from both chambers have been made, and the $\frac{SiO_2}{Fe_2O_3}$ ratios calculated. Iron moves both to the anode and cathode during

[2] TOTH, S. J. Unpublished data, New Jersey Agricultural Experiment Station.

electrodialysis, as indicated by the data. The reason for this has been previously noted. The higher average molar $\frac{SiO_2}{Fe_2O_3}$ ratio in the anode chamber (average 43.8) compared to the cathode (average 23.5) must be attributed in part to the lower iron and higher silica content. It should be pointed out, however, that more iron was found in the cathode chamber (0.53 mgm.) than in the anode chamber (0.33 mgm.).

A series of cylinder experiments at the New Jersey Agricultural Experiment Station on a Sassafras loam that has been receiving different amounts of organic matter yearly in the form of rye straw for the past 12 years also presented an excellent opportunity for base exchange studies (3). The particular cylinders chosen for study received the following special treatments yearly:

TABLE 4

Comparison of the quantities of iron in dialyzates from certain soils and the $\frac{SiO_2}{Fe_2O_3}$ *ratio in the dialyzates*

PLOT	TOTAL Fe_2O_3 IN DIALYZATES		$\frac{SiO_2}{Fe_2O_3}$* RATIOS IN	
	Cathode chamber	Anode chamber	Cathode chamber	Anode chamber
	mgm.	*mgm.*		
7 A	0.65	0.16	16.5	41.0
7 B	0.47	0.37	21.3	44.0
5 A	0.60	0.39	17.1	37.9
5 B	0.77	0.34	26.0	68.5
18 A	0.46	0.57	23.5	42.1
18 B	0.61	0.31	26.5	75.7
19 A	0.36	0.15	18.6	36.0
19 B	0.34	0.32	29.0	45.5
Average.....	0.53	0.33	23.5	43.8

* Molar ratio.

Cylinder Number	*Special Treatment*
141 and 142	No organic matter
143 and 144	Rye straw cut fine, 1 ton to the acre
145 and 146	Rye straw cut fine, 2 tons to the acre
147 and 148	Rye straw cut fine, 4 tons to the acre
149 and 150	Rye straw cut fine, 8 tons to the acre

The straw was worked into the soil to a depth of 4 to 5 inches just before planting. Each cylinder received 20 gm. of superphosphate (640 pounds an acre) and 10 gm. muriate of potash. The standard application of nitrate of soda was 10 gm. for a cylinder, but in certain years additional nitrate of soda was applied.

In general the data obtained on the cylinder soils (table 5) were not so defi-

nite and clear-cut as those obtained from the field plots. It must be pointed out at the start that the condition of the organic matter in the cylinder soils was markedly different from that in the field plots. In the latter, the added organic matter in the form of manure was in a relatively well-advanced stage of decomposition, whereas in the former the organic matter additions in the form of rye straw were not well decomposed. Although over a period of years some of this rye straw was decomposed, when the samples were taken for this work a considerable amount could still be identified. It is also a well-known fact that rye straw is notoriously poor in bases, whereas, on the other hand, the manure used in the field plots was fairly high in basic constituents.

The carbon content of these soils is given in table 6. It will be noted that there is only slight increase until the 8-ton application is reached. This shows about 0.5 per cent increase over the check.

TABLE 5

Electrodialyzable bases in cylinder soils

Sassafras loam

CYLINDER NO.	TREATMENT	TOTAL BASES DIALYZED	BASES IN DIALYZATE FRACTIONS			
			0–6 hr.	6–14 hr.	14–30 hr.	30–54 hr.
		m.e.	*m.e.*	*m.e.*	*m.e.*	*m.e.*
141 and 142	Check	4.913	2.633	1.567	0.512*	0.201*
143 and 144	2,000 pounds rye straw‡	4.134	2.353	1.580	0.201†	0.000†
145 and 146	4,000 pounds rye straw	4.120	2.914	1.206	0.000†	0.000*
147 and 148	8,000 pounds rye straw	5.506	3.135	1.588	0.603*	0.180†
149 and 150	16,000 pounds rye straw	4.904	3.256	1.648*	0.000†	0.000†

* Slight sediment
† Heavy sediment } reddish brown in color.
‡ On the acre basis.

The quantity of bases delivered from these soils is very irregular. The discrepancies in the total dialyzable bases from the cylinder soils may be due to the bases adsorbed by the sediment found in the cathode chamber. This sediment contained as much as 0.17 m.e. CaO and 0.53 m.e. MgO, which were not titrable when the total bases were being determined. However, the delivery of bases at different time intervals was very similar to that found in field experiments, namely, that the bulk of the bases were set free during dialysis in 14 hours. After the removal of the bulk of strong bases, a heavy sediment appeared in the cathode chamber.

The ultimate pH values given in table 6 show only a slight reduction as the organic matter applications increase. The check cylinder was 4.48, whereas the highest organic matter treatment gave only 4.30. This reduction in the ultimate pH can be correlated in general with a slight increase in carbon content of these cylinders. The unsaturation values show slight variations, but no definite conclusion can be drawn.

From a consideration of the cation exchange values, also recorded in table 6, it can be seen that only on the cylinders receiving the highest organic matter was the cation exchange capacity before electrodialysis higher than on the check cylinder. Similar results are to be noted with these samples after electrodialysis, but electrodialysis has reduced the cation exchange capacity as in the case of the field plots.

TABLE 6

Data on cylinder soils with varying organic matter treatments

TREATMENT	FIELD pH	ULTIMATE pH	CARBON CONTENT OF SOILS	EXCHANGEABLE HYDROGEN PER 100 GM. SOIL BY BARIUM ACETATE	UNSATURATION	CATION EXCHANGE CAPACITY PER 100 GM. SOIL BY BARIUM ACETATE		
						Before electrodialysis	After electrodialysis	Difference
			per cent	*m.e.*	*per cent*	*m.e.*	*m.e.*	*m.e.*
Check	6.30	4.48	1.23	0.92	10.2	9.01	7.68	1.33
2,000 pounds rye straw	6.30	4.46	1.19	0.85	9.9	8.66	7.63	1.03
4,000 pounds rye straw	6.42	4.45	1.34	1.16	13.6	8.54	7.77	0.77
8,000 pounds rye straw	6.49	4.45	1.36	1.28	13.5	8.69	7.77	0.92
16,000 pounds rye straw	6.53	4.30	1.75	1.34	14.2	9.40	8.28	1.12

TABLE 7

Amounts of iron and silica dialyzable in relation to the ultimate pH

CYLINDER NO.	TREATMENT	TOTAL Fe_2O_3 DIALYZED	TOTAL SiO_2 DIALYZED	ULTIMATE pH
		mgm.	*mgm.*	
141 and 142	Check	0.36	5.7	4.48
143 and 144	2,000 pounds rye straw*	0.65	7.0	4.46
145 and 146	4,000 pounds rye straw	0.42	5.9	4.45
147 and 148	8,000 pounds rye straw	0.32	7.9	4.45
149 and 150	16,000 pounds rye straw	1.04	8.8	4.30

* On the acre basis.

An increase in the acidic nature of the soil complex indicates a greater mobilization of iron, aluminum, and silica (11). That this is true in general can be seen from table 7, where the total iron and silica in the cathode sediment is presented. The cylinder with the lowest ultimate pH (4.3) yields the greatest quantity of silica (8.8 mgm.) and iron (1.04 mgm.), whereas the check cylinder, with an ultimate pH of 4.5, yielded only 5.7 mgm. of silica and 0.36 mgm. of iron.

At the completion of the electrodialysis of the soil sample receiving the highest amount of rye straw (cylinders 149 and 150), the pH values from three

different soil points in the center compartment were determined. These points and pH values were as follows:

	pH
Soil near the cathode (0 to 0.4 cm.)	5.00
Soil near the center	4.60
Soil near the anode (0 to 0.4 cm.)	4.32

These results indicate that a definite pH gradient exists in the soil compartment and further show that the soil complex near the cathode membrane has become enriched in the basoid fractions, and therefore its ultimate pH has increased and its cation exchange capacity has decreased. On the other hand, the soil near the anode has become enriched in the acidoid fractions, and its ultimate pH is lower and its cation exchange capacity is greater than the original soil complex.

An analysis of the cathode sediment should give an indication of the nature of the soil complexes near the cathode parchment and should indicate whether or not the cathode sediment is becoming more basic in nature. The analysis of the sediment was as follows:

Weight of sediment from 100 gm. soil	175.6 mgm.*
Cation exchange capacity per gram	0.13 m.e.*
Loss on ignition	25.56 per cent*
Water	7.60 per cent*
Carbon	5.95 per cent*
Organic matter by factor (1.724)	10.23 per cent*
Constituents in the ash	
SiO_2	7.58 per cent
Fe_2O_3 and Al_2O_3	26.89 per cent
Mn_3O_4	24.61 per cent
CaO	3.60 per cent
MgO	8.23 per cent

* Oven-dry basis.

The appearance of organic matter in the sediment no doubt means that humus has moved in combination with cations as electropositive micellae. The surprisingly high content of manganese (24.61 per cent of the ash) indicates that this cation has moved in a similar manner to that described for iron and aluminum. The most interesting fact in connection with the analysis of the sediment is that the material is predominantly basic and has a low cation exchange capacity (0.13 m.e. per gram). Also, appreciable amounts of calcium and magnesium were found. This must mean either that calcium and magnesium, in combination with acidoids, move as an electropositive micella, or that when the complexes of iron, aluminum, silica, organic matter, and manganese passed into the cathode chamber, calcium and magnesium were adsorbed from the liquor in this chamber during precipitation. The fact remains, however, that these bases present in the sediment were not titrable.

It was found at the completion of the electrodialysis of the cylinder soils

that a layer of precipitated material had accumulated on the cathode parchment paper facing the soil mass. This layer was brownish in color and mottled with numerous white particles. Further work is being done on this layer, especially with respect to its chemical composition in comparison to the chemical composition of the colloidal fraction from these soils.

SUMMARY

Certain field plots and cylinder soils at the New Jersey Experiment Station receiving various amounts of organic matter were electrodialyzed. The influence of organic matter additions upon titrable acids and bases; upon ultimate pH; upon cation exchange capacity; and upon mobilization of iron, silica, and phosphorus was studied.

It was shown that the quantity of bases electrodialyzed is not a function of the pH of the field sample, but rather depends upon the total cation exchange capacity and the degree of base saturation.

The total dialyzable acids and bases were greater on the limed than on the unlimed plots, and still greater on those plots receiving manure and lime.

The bulk of the bases and acid were delivered in 14 hours.

The addition of organic matter and phosphorus to the soil increased the acidoid-basoid ratio of the soil complex, and consequently lowered the ultimate pH and increased the cation exchange capacity. Thus the plots receiving manure showed a decrease of approximately 0.4 to 0.6 pH unit and an increase in cation exchange capacity of about 4 m.e. per 100 gm. of soil.

Mobilization of iron and silica increased with decreasing ultimate pH.

Electrodialysis reduced the cation exchange capacity of all samples, the greatest loss occurring with the samples from plots receiving manure and lime. This was explained on the basis that during electrodialysis acidoids were hydrolyzed, and also that a certain fraction of the soil complexes mobilized and precipitated in the cathode chamber.

The average silica-iron ratio in the dialyzate from the anode was higher than that from the cathode.

The degree of the decomposition of the organic matter was found to influence the colloidal properties previously listed, i.e. with the cylinder soils receiving undecomposed rye straw only slight effects were noted.

It was found that after electrodialysis a pH gradient varying from 4.3 near the anode to 5.0 at the cathode existed in the soil compartment.

An analysis of the sediment appearing in the cathode dialyzates showed that the material was predominantly basic and had a low cation exchange capacity. Organic matter and manganese, as well as appreciable quantities of calcium and magnesium, were also found in the sediment.

REFERENCES

(1) Anderson, M. S., and Byers, H. G. 1933 Character and behavior of organic soil colloids. U. S. Dept. Agr. Tech. Bul. 377.

(2) Anderson, M. S., and Mattson, S. 1926 Properties of the colloidal soil material. U. S. Dept. Agr. Bul. 1452.

(3) BLAIR, A. W., AND PRINCE, A. L. 1933 Influence of organic matter on the crop yield and on carbon-nitrogen ratio and nitrate formation in the soil. *Soil Sci.* 35: 209–219.

(4) LIPMAN, J. G., BLAIR, A. W., AND PRINCE, A. L. 1928 Field experiments on the availability of nitrogenous fertilizers, 1923–1927. *Soil Sci.* 26: 1–25.

(5) LÖDDESÖL, A. 1932 Factors affecting the amount of electrodialyzable ions liberated from some soils. *Soil Sci.* 33: 187–211.

(6) MCGEORGE, W. T. 1930 The base exchange property of organic matter in soils. Univ. Ariz. Agr. Exp. Sta. Tech. Bul. 30.

(7) MCGEORGE, W. T. 1931 Organic compounds associated with base exchange reactions in soils. Univ. Ariz. Agr. Exp. Sta. Tech. Bul. 31.

(8) MATTSON, S. 1926 Electrodialysis of the colloidal soil material and the exchangeable bases. *Jour. Agr. Res.* 33: 552–567.

(9) MATTSON, S. 1930, 1931 Laws of soil colloidal behavior: III, IV. Isoelectric precipitates. *Soil Sci.* 30: 459–495 (1930); 31: 57–77 (1931).

(10) MATTSON, S. 1931 Laws of soil colloidal behavior: V. Ion adsorption and exchange. *Soil Sci.* 31: 311–331.

(11) MATTSON, S. 1933 Laws of soil colloidal behavior: XI. Electrodialysis in relation to soil processes. *Soil Sci.* 36: 149–163.

(12) MATTSON, S. 1936 The pH and base saturation of a podzol profile. *Third Internatl. Cong. Soil Sci.* 1: 67–70.

(13) MULLER, J. F. 1930 The base exchange capacity of organic materials. Thesis, Rutgers University.

(14) PIERRE, W. H., AND SCARSETH, G. D. 1931 Determinations of the percentage base saturation of soils and its value in different soils at definite pH values. *Soil Sci.* 31: 99–114.

(15) PRINCE, A. L., AND TOTH, S. J. 1936 The effect of phosphates on the cation exchange capacity of certain soils. *Soil Sci.* 42: 281–290.

(16) TIULIN, A. T. 1926 Decomposition of organic matter and changes in nitrification and adsorption power of soils. Trans. Sci. Inst. Fert. Moscow 33.

(17) TIURIN, I. V. 1931 New modification of the volumetric method of determining soil organic matter by means of chromic acid. *Pedology* 26–36–47.

(18) WAKSMAN, S. 1936 Humus. Williams and Wilkins, Baltimore, Md.

(19) WAKSMAN, S., AND IYER, K. R. 1932 Contributions to our knowledge of the chemical nature and origin of humus: I. On the synthesis of the humus nucleus. *Soil Sci.* 34: 43–70.

SAMPLING SOIL FOR THE pH DETERMINATION

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While conducting soil treatment experiments for the control of brown rot of potatoes at Hastings, Florida, it has been necessary to determine, by the quinhydrone method, the pH value of thousands of samples of soils which were treated with various agents to make them acid or alkaline. During the progress of this work, the junior author designed and constructed a soil sampler which has proved to be very useful and convenient in taking samples from the upper 8 inches of sandy soils.

As constructed, the sampler consists of two blades made of sections cut lengthwise from a piece of $1\frac{1}{2}$-inch steel tubing $\frac{1}{16}$ inch thick, and a handle

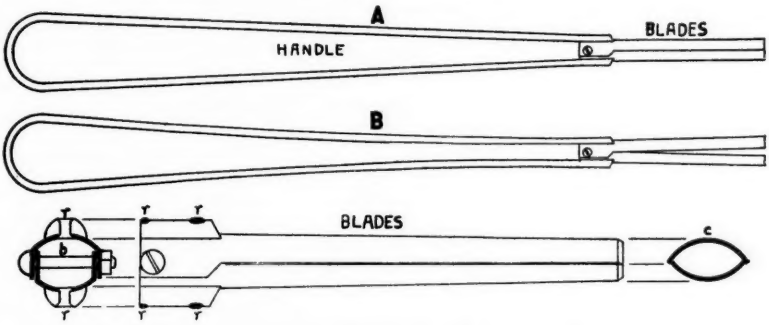

FIG. 1. DIAGRAM SHOWING THE DIFFERENT PARTS OF THE SOIL SAMPLER

made from $\frac{5}{8}$-inch half-round spring steel which is bent and fitted to the blades, as shown in figure 1, A. The handle is 26 inches in length, and the blades, 8 inches. The handle and blades are fastened together with rivets (*r*), and the blades are held in position with a stove bolt (*b*) which passes through the two overlapping ends at the top. The blades are sharpened at the lower end to cut into the soil and when in position the sampler will remove a core of soil $\frac{5}{8}$ inch by 1 inch in cross section (*c*). To draw a sample, the handle is grasped at the upper end and the blades are plunged or shoved into the ground. The instrument is then withdrawn from the soil and the sample can be released

and deposited in a container by pressing the sides of the handle together (*B*), which forces the blades apart, permitting the sample to drop out.

Milk bottles are good containers for the soil samples. After a sample is deposited in a bottle, it can be sealed with a milk-bottle cap on which is written a symbol that will serve to identify the sample. When the sample is taken to the laboratory, it can be prepared for the pH determination by removing the cap, adding the required amount of distilled water, replacing the cap and then shaking the bottle. Bottles can be transported to and from the field in crates; a milk-bottle carrier is a convenient container for the bottles while the samples are being drawn. Half-pint, pint, and quart bottles should be available, depending upon the size of the samples drawn from representative areas in the field.

The sampler and the procedure described for the preparation of the samples for the pH determination are particularly adapted for use in those sections of the country where the soils are similar to the sandy types of Florida but could not be used successfully where the soils have a clay texture or contain gravel or stones.

A PEDOLOGIC STUDY OF SOME SOILS IN NEW JERSEY[1]

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The soil survey of New Jersey was completed just about the time when the pedologic approach to the study of soils began to assume significance. The soil samples taken by the soil survey for analyses and those that had been analyzed represent arbitrary depths with no consideration for the inherent constitutional characteristics and properties of the soil body. As a result, the chemical data do not fully characterize the soils, and the expected information is not so broad and enlightening as anticipated.

A similar procedure was, until recently, followed elsewhere in the United States, and the results were similar. Very few analyses of soils of the United States on the profile basis are on hand. This is very strikingly exemplified in the classical work of the late Doctor Marbut (14).

In the report following, total analyses of the most important and most prevalent soils of New Jersey are presented. Unfortunately, not all the determinations desired have been made. The large number of samples which must be taken on the profile basis complicate matters, and the shortcomings are to be attributed to this factor.

The data on the analyses of the soils in New Jersey are not to be looked upon as of "local" soils. They may be relegated also to all the soils of the zone to which they belong and which are geographically distributed outside the boundaries of the state.

From the broad aspects of soil classification, the soils under consideration are the brown forest podzolic soils of the humid temperate zone. This position in the classification system placards these soils with definite characteristics which to the student of soils mean certain behavior and probable response, in terms of crops, to treatment.

The detailed analyses of the data of the soil profile offer a clear-cut picture of the translocation and movement of the soil constituents. This knowledge may serve as a guide to the fertilizer practices and to the reactions which might take place upon the addition of certain constituents. The complete analyses also give an inventory of the fertility resources of the soils.

The soils investigated were sampled in forested areas that have never been cultivated, except for the Hagerstown soil, which was sampled from a plowed field.

[1] Journal Series paper of the N. J. Agricultural Experiment Station, department of soil chemistry and bacteriology.

GEOGRAPHIC AND GEOLOGIC FEATURES

The soils under consideration originated from parent material in two geographic and geologic provinces; first, the Coastal Plain which borders the Atlantic from the Gulf of Mexico to the Hudson and which is represented northward to Massachusetts Bay by several islands and the peninsula of Cape Cod, and secondly, the Appalachian province which extends from the Coastal Plain westward to the Mississippi lowland and from central Alabama northeastward into Canada.[2]

Of the 13 soil series discussed in this paper, the parent material of some belongs to the geologic division of the Appalachian Mountains, the Highlands; that of one (the Penn silt loam), to the Piedmont; and that of others, to the Coastal Plain.

The Highlands consist primarily of metamorphosed rock of pre-Cambrian age. As described by Lewis and Kümmel (12), "... the rocks consist of gneisses and schists, possibly in part of sedimentary origin, with some marble or crystalline limestone and of intrusive igneous rocks, for the most part gneissoid.... Infolded with the pre-Cambrian crystalline rocks and for the most part occupying the narrow valleys that separate the ridges of the Highlands are strips of more or less metamorphosed Paleozoic strata."

The Piedmont on which the Penn silt loam under consideration is located consists of Triassic rocks—shale.

The Coastal Plain consists of formations of unconsolidated almost horizontal beds of gravel, sand, sandy clay, and marls with a slight dip to the coast. These formations are chiefly Tertiary, the upper Miocene.

Glacial drift, both stratified and unstratified, greatly antedating the moraines of the Wisconsin stage of glaciation occurs in the Appalachian Valley and Piedmont regions.

TOPOGRAPHY

The Appalachian Mountain division, the Highlands, has an average elevation of 1,000 feet above sea level. Its topography is hilly with flat-topped ridges separated by narrow valleys.

The Piedmont is a sort of dissected plateau with knobs and ridges, which are more prominent inland, and a low plain which is more or less hilly and which, in the vicinity of Newark Bay, falls to sea level.

The Coastal Plain represents a gentle slope, 5 to 6 feet per mile, toward the Atlantic. Its topography is thus level with slight undulations.

CLIMATE

The entire area under consideration is in the humid temperate zone, but within the area there are some minor climatic differences. Thus, the Coastal

[2] The references to the geographic and geologic features were taken from the work of Lewis and Kümmel (12).

Plain has a slightly milder climate than the Piedmont or Appalachian, due to the modifying influences of the Atlantic Ocean and the lower elevation.

The mean annual temperature varies from 53 to 54°F. in the Coastal Plain to 48° in the Appalachian Valley with even lower temperatures at higher elevations. Not only is the mean temperature somewhat different in the sections of the area, but the range of temperature during the seasons varies considerably. Thus in some areas a temperature of −19°F. has been re-

TABLE 1

*Chemical analysis of Sassafras and Collington loams**

LABORATORY NUMBER OF SAMPLE	HORIZON	DEPTH	SiO_2	Fe	Al	Ca	Mg	Mn	N	P	REACTION		CATION EXCHANGE CAPACITY†	UNSATURATION (H)	
											H_2O extract	Neutral salt extract			
		cm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*pH*	*pH*	*m.e.*	*m.e.*	*per cent*
							Sassafras loam								
1	A_0	3–4	76.05	2.187	2.784	0.249	0.285	.....	0.373	0.054	5.0	3.8	22.30	19.70	88.3
2	A_1	15	85.33	2.887	2.647	0.177	0.289	0.014	0.038	0.035	5.2	4.4	5.46	5.14	94.1
3	A_2	18	85.78	3.2	4.529	0.326	0.369	0.225	0.032	0.037	5.0	4.4	4.74	4.27	93.6
4	B_1	13.5	84.35	3.2	3.407	0.367	0.380	0.162	0.024	0.044	5.1	4.4	4.98	4.05	81.3
5	B_2	16.5	84.30	3.317	3.536	0.242	0.410	0.114	0.016	0.039	4.9	4.5	5.2	4.05	78.0
6	C_1	.....	87.72	3.675	2.256	0.252	0.388	0.135	0.008	0.040	5.0	4.6	.....	.....	....
							Collington loam								
53	A_0	3	60.28	2.230	1.745	0.332	0.291	0.234	0.912	0.099	4.9	4.0	56.73	34.5	60.8
54	A_1	9	84.15	2.565	2.693	0.189	0.276	0.054	0.113	0.073	4.7	4.4	16.21	8.4	51.8
55	A_2	23	85.44	2.962	3.078	0.200	0.316	0.108	0.035	0.048	5.0	4.4	5.64	3.8	67.3
56	B_1	18	79.69	4.182	3.758	0.182	0.420	0.130	0.026	0.067	4.9	4.4	8.34	4.85	58.1
57	B_2	26	79.56	4.600	3.372	0.157	0.468	0.162	0.017	0.066	4.9	4.4	9.58	5.4	56.3
58	C_1	13	80.58	5.157	2.657	0.163	0.503	0.122	0.013	0.067	4.9	4.4	9.28	5.2	56.0
59	C_2	.....	84.89	4.739	1.591	0.150	0.415	0.148	0.007	0.032	4.9	4.4	7.04	3.5	49.7

* The soil material was prepared for analyses and analyzed according to the methods of the Association of Official Agricultural Chemists (A. O. A. C.).

† The cation exchange capacity was determined at pH 7.0 with Ba-acetate. The unsaturation was determined by titrating the Ba-acetate extract with 0.02 *N* KOH to pH 7.0.

corded, whereas in others the temperature has not fallen below +2°. These temperature differences have not as yet been evaluated from the standpoint of the soil.

The rainfall also varies from 41 to 51 inches, again primarily as a result of topography and relation to movements and direction of winds. These precipitation differences have not as yet been evaluated.

In general the minor climatic variations and their influence on the movement

and translocation of the soil constituents need elucidation, but not until we have on hand reliable lysimeter data will it be possible to trace the influence of these minor climatic differences.

In presenting the data on the chemical analyses of the more important soils in New Jersey the system of the U. S. Soil Survey of dividing the soils into

TABLE 2

Chemical analysis of Washington, Dover, and Dutchess loams

LABORATORY NUMBER OF SAMPLE	HORIZON	DEPTH	SiO_2	Fe	Al	Ca	Mg	Mn	N	P	REACTION: H_2O extract	REACTION: Neutral salt extract	CATION EXCHANGE CAPACITY	UNSATURATION (H)	
		cm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*pH*	*pH*	*m.e.*	*m.e.*	*per cent*
							Washington loam								
17	A_0	4–5	61.40	4.098	5.318	0.760	0.470	0.234	0.399	0.076	7.2	...	37.20	1.98	5.3
18	A	21	71.57	4.644	5.957	0.254	0.395	0.184	0.067	0.050	5.3	4.4	12.00	5.97	50.0
19	B_1	11	69.12	5.405	6.717	0.204	0.384	0.198	0.048	0.057	5.1	4.4	8.16	5.37	65.8
20	B_2	19	65.55	5.894	6.995	0.154	0.349	0.198	0.019	0.058	5.3	4.4	6.24	3.19	51.1
21	C	.....	66.30	5.992	6.817	0.170	0.418	0.132	0.008	0.056	5.4	4.8	5.03	2.2	43.7
							Dover loam								
40	A_1	2	74.5	3.011	4.160	0.450	0.743	0.061	0.147	.....	6.6	6.8	26.84	0.4	1.4
41	A_2	4	75.5	2.943	4.966	0.356	0.749	0.081	0.122	.....	6.4	6.8	20.7	0.8	3.8
42	A_3	18	77.3	2.990	5.289	0.289	0.756	0.091	0.048	.....	5.8	6.2	5.14	1.95	37.9
43	B_1	22.5	73.3	3.903	5.289	0.276	0.592	0.100	0.037	.....	6.4	6.6	9.1	1.3	14.2
44	B_2	14	69.0	4.604	6.523	0.314	0.626	0.145	0.044	.....	6.4	6.6	11.2	1.1	9.8
45	C_1	15	.....	.....	.....	.....	.....	.....	0.015	.....	7.2	7.4	11.6	....	....
46	C_2	.....	.....	.....	.....	.....	.....	.....	0.022	.....	7.4	7.6	13.17	....	....
							Dutchess loam								
47	A_0	4	54.88	3.345	5.542	1.770	1.663	0.032	0.448	0.089	5.8	6.2	34.6	5.25	15.2
48	A_1	4	59.44	3.504	5.786	0.619	0.942	0.072	0.383	0.073	6.8	7.4	34.2	....	....
49	A_2	14	64.43	3.484	6.166	0.525	1.103	0.036	0.221	0.045	5.4	5.6	22.1	4.65	21.0
50	B_1	16	64.77	4.628	6.864	0.338	1.121	0.144	0.122	0.061	5.8	6.0	13.8	2.45	17.7
51	B_2	19	63.96	5.018	7.616	0.313	1.436	0.137	0.072	0.052	6.1	6.2	12.5	1.3	10.4
52	C	.....	71.49	4.600	6.033	0.250	1.092	0.063	0.033	0.069	6.4	6.8	13.67	0.3	2.1

series was utilized. The superimposing of the soil series—which mean certain defined characteristics—on the broad fundamental pedogenic basis may lead to a more rational appreciation of the soils.

In tables 1 to 5 the analyses of the soils are given. Some of these have been reported in earlier publications (4, 7, 10) where the methods of sampling and preparation of material for analyses were given. They are repeated here, with

some additional data, grouped, and compared with the analyses of other soils, thereby elucidating more thoroughly the nature of the soils.

DEPTH OF PROFILE

A horizon

A comparison of the soils formed from Coastal Plain parent material (table 1) with those formed from Appalachian Mountain and Valley parent material (table 2) shows a definite trend of profile development in the soils of the two geographic and geologic areas. The A horizon of the Sassafras and Collington

TABLE 3

Chemical analysis of Chester and Gloucester gravelly loams

LABORATORY NUMBER OF SAMPLE	HORIZON	DEPTH	SiO_2	Fe	Al	Ca	Mg	Mn	N	P	REACTION: H_2O extract	REACTION: Neutral salt extract	CATION EXCHANGE CAPACITY	UNSATURATION (H)	
		cm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*pH*	*pH*	*m.e.*	*m.e.*	*per cent*
						Chester gravelly loam									
22	A_0	4	63.20	3.805	5.731	0.594	0.369	0.144	0.270	0.056	6.4	5.0	18.5	5.83	31.5
23	A_1	12	71.45	4.488	5.656	0.495	0.404	0.157	0.071	0.040	5.5	4.4	7.19	4.57	63.5
24	A_2	16	72.55	4.995	5.210	0.526	0.442	0.198	0.036	0.043	5.4	4.4	6.31	3.46	54.8
25	B_1	15	68.37	6.497	5.572	0.417	0.464	0.248	0.025	0.045	5.2	4.4	6.8	4.49	66.0
26	B_2	43	63.25	10.194	5.935	0.260	0.158	0.212	0.013	0.047	5.2	4.4	6.6	3.34	50.5
27	C	.....	68.92	5.277	5.814	0.404	0.182	0.243	.....	0.029	5.4	4.6	5.3	2.38	45.0
						Gloucester gravelly loam									
34	A_0	3	53.5	2.498	4.558	0.540	0.435	0.207	0.499	.....	...	...	49.0	36.97	75.4
35	A_1	19.5	65.3	3.005	6.086	0.557	0.494	0.239	0.188	.....	4.9	4.4	19.4	15.36	79.2
36	A_2	29.5	74.4	4.410	5.472	0.543	0.618	0.207	0.058	.....	4.8	4.4	8.3	7.49	90.2
37	B_1	15	72.8	4.100	3.572	0.573	0.614	0.072	0.043	.....	5.0	4.6	9.8	5.87	59.9
38	B_2	26	72.7	4.088	4.536	0.557	0.639	0.059	0.036	.....	5.0	4.6	8.8	5.98	67.9
39	C_1	.....	70.4	5.855	4.980	1.018	0.978	0.207	0.027	.....	5.0	4.5	5.7	3.39	59.5

loams is deeper than the corresponding horizon of the Washington, Dover, and Dutchess loams. The average depth of the loams on the Coastal Plain is from 12 to 14 inches, or 30 to 35 cm., whereas the depth of the loams of the Appalachian Mountain or Valley is from 9 to 10 inches, or 22 to 26 cm.

From the pedologic point of view the variation in depth of soils of similar mechanical composition indicates degree of maturity. The Coastal Plain soils are more mature than those of the Appalachian Mountain and Valley soils. The reason for the comparative youth or immaturity of the latter is not the climate, even though there are some minor differences between the

climate of the northern part (Appalachian) of the state and that of the southern, as has been pointed out. The real cause of the difference in the depth of the A horizon is the element of topography; in other words, the soils of the northern part are orogenic[3] in nature. The hilly topography is conducive to the mechanical removal of some of the A horizon. Although in a way this may be called "erosion," it is not erosion in the sense in which the term is now being employed.

An examination of the gravelly loams (table 3) shows that the A horizon is somewhat deeper than that of the ordinary loams in a similar topographic

TABLE 4

Chemical analysis of Penn and Hagerstown silt loams

LABORATORY NUMBER OF SAMPLE	HORIZON	DEPTH	SiO_2	Fe	Al	Ca	Mg	Mn	N	P	REACTION		CATION EXCHANGE CAPACITY	UNSATURATION (H)	
											H_2O extract	Neutral salt extract			
		cm.	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	pH	pH	m.e.	m.e.	per cent
Penn silt loam															
7	A_0	3–4	52.55	4.252	9.009	0.532	1.043	0.321	0.367	0.057	5.2	4.3	26.4	18.64	70.6
8	A	12.0	57.85	5.697	9.588	0.217	1.054	0.351	0.143	0.031	4.9	4.5	14.1	7.56	53.6
9	B_1	26.0	35.70	5.970	10.348	0.244	1.051	0.171	0.049	0.024	4.8	4.5	10.7	7.56	70.6
10	B_2	38.0	54.97	6.672	10.772	0.148	1.201	0.306	0.027	0.020	4.9	4.3	11.4	7.56	66.3
11	C	....	55.10	6.440	10.678	0.148	1.306	0.315	0.024	0.024	5.1	4.3	11.2	7.64	68.2
Hagerstown silt loam															
12	A_p*	24	70.875	3.162	6.418	0.45	0.483	0.221	0.146	0.086	7.4	6.5	13.00	0.709	5.4
15	A_2	4	72.375	2.642	7.107	0.513	0.595	0.324	0.076	0.052	7.6	6.7	7.00	0.678	9.6
13	B_1	21	69.375	3.712	7.789	0.484	0.661	0.108	0.044	0.046	7.4	6.6	7.50	0.56	7.4
14	B_2	21	54.048	6.697	10.023	0.536	0.979	0.234	0.046	0.076	7.6	6.6	18.32	0.40	2.1
16	C	....	44.825	6.592	9.630	3.456	2.503	0.486	0.052	0.083	7.8	7.2	22.37	0.00	0.00

* The samples of this soil were taken from a cultivated area, hence the A_p—plowed layer—designation.

position; especially is this true with respect to the Gloucester gravelly loam. This particular soil was noted for its gritty material and was lighter in texture than the average loam. This might explain the deeper A horizon, for it is known that light-textured soils have a deeper horizon of eluviation.

The A horizon of the silt loams (table 4) shows a depth similar to that of the loams. In the case of the Penn (Piedmont region on a level topography), it is the orogenic nature of the soil which determines its profile, and it is probable that other normal climatogenic soils of a similar mechanical composition may have a similar or deeper depth of the horizon of eluviation. As to the

[3] For a full discussion of orogenic soils the reader is referred to the treatise "Pedology" (9).

Hagerstown, which is of the Appalachian area, the topography, to which reference was made in the discussion of the loams, and even more so the

TABLE 5

Chemical analysis of Sassafras fine sandy loam, glei podzolic, Lakewood fine sand, and Sassafras sand

LABORATORY NUMBER OF SAMPLE	HORIZON	DEPTH	SiO_2	Fe	Al	Ca	Mg	Mn	N	P	REACTION		CATION EXCHANGE CAPACITY	UNSATURATION (H)	
											H_2O extract	Neutral salt extract			
		cm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*pH*	*pH*	*m.e.*	*m.e.*	*per cent*
						Sassafras fine sandy loam									
60	A_0	3	67.89	1.032	2.646	0.094	0.082	0.036	0.490	0.038	4.6	4.6	37.68	27.35	72.3
61	A_1	4	90.49	1.506	2.630	0.013	0.093	0.063	0.048	0.019	4.8	4.6	9.72	3.04	31.2
62	A_2	6	91.26	1.812	2.369	T	0.053	0.050	0.025	0.007	4.6	4.4	8.20	3.04	37.1
63	A_3	14	87.50	1.951	3.655	0.016	0.090	0.004	0.034	0.007	4.7	4.6	7.60	4.46	58.7
64	B_1	15	86.19	1.450	4.013	T	0.123	0.040	0.016	0.007	5.2	4.6	6.68	2.13	31.9
65	B_1	25	88.30	1.896	3.921	0.025	0.147	0.099	0.009	0.009	5.2	4.8	6.08	1.52	25.0
66	B_2	15	87.12	1.924	3.995	0.015	0.139	0.054	0.005	0.012	4.8	4.8	7.29	1.57	21.5
67	C	.....	91.73	1.944	1.316	0.025	0.147	0.086	0.026	0.001	5.1	4.9	.....	0.61	....
						Intermediate between Collington and Shrewsbury—glei podzolic									
74	A_1	10	84.79	1.469	0.730	0.189	0.115	0.137	0.137	.....	5.2	4.2	14.38	13.17	91.6
75	A_2	25	90.69	2.448	0.917	0.154	0.164	0.196	0.042	.....	5.4	4.6	6.36	3.67	57.7
76	B	15	83.82	4.354	1.352	0.135	0.170	0.203	0.054	.....	5.1	4.4	9.56	6.55	68.5
77	G	.....	84.23	3.602	1.633	0.132	0.219	0.262	0.056	.....	4.9	4.6	9.9	8.45	85.4
						Lakewood fine sand									
78	A_1	13	97.17	0.909	0.216	0.084	0.044	.....	0.014	.....	4.8	4.4	3.00	2.0	66.6
79	A_2	25	98.12	0.769	0.167	0.087	0.048	.....	0.004	.....	4.8	4.8	0.77	0.55	71.4
80	B_1	20	93.32	1.329	1.325	0.089	0.067	.....	0.022	.....	5.1	5.0	2.74	2.60	94.8
81	B_2	35	93.40	1.329	1.405	0.145	0.070	.....	0.017	.....	5.2	5.0	2.74	2.55	93.0
82	C	.....	95.95	0.944	1.107	.....	.....	.....	0.006	.....	5.2	5.2	0.64	0.5	78.1
						Sassafras sand									
28	A_0	3	71.75	1.920	0.687	0.360	0.064	0.194	0.194	0.041	4.9	...	12.32	11.12	90.3
29	A_1	10	94.92	2.028	0.470	0.244	0.048	0.167	0.023	0.028	4.9	4.3	2.7	2.5	92.6
30	A_2	15	96.40	2.147	0.327	0.201	0.042	0.126	0.009	0.028	5.0	4.4	1.43	1.23	86.0
31	A_3	21	94.32	2.731	0.323	0.248	0.052	0.171	0.011	0.027	5.3	4.6	0.85	.....	....
32	B	28	93.32	3.231	0.396	0.23	0.060	0.072	0.013	0.025	5.1	4.6	2.02	1.5	74.2
33	C	.....	93.42	3.584	0.196	0.244	0.036	0.068	0.006	0.024	5.4	4.6	1.67	1.2	71.9

nature of the parent material (again an orogenic feature), the limestone, may have some bearing on the depth of the A horizon.

The A horizon of the light-textured soils of the Coastal Plain (table 5) is relatively deep for the simple reason that the coarser fractions admit more efficient percolation and the storehouse of eluviable material is comparatively scant

Attention is directed to the lack of data on the A_0 for three of the soils analyzed. In two cases, the samples were lost in the process of analysis. In the case of the Lakewood (table 5), no A_0 was found—one of the rare phenomena encountered in virgin soils, a discussion of which may be found elsewhere (11).

B horizon

The depth of the B horizon in soils of similar mechanical composition is not the same, as may be judged from the data in the respective tables, but depends in a large measure on the composition of the parent material. If the parent material is rich in bases, the process of podzolization, which determines the movement and translocation of the soil constituents, is impeded. Under such conditions the B horizon does not get many products of the eluviation process. On the other hand, if the resistance of the parent material to the podzolization reactions had been overcome, i.e., the excess supply of bases had been exhausted from the A horizon, the B horizon will be deep. The presence of the bases in the B tends to precipitate the soluble materials coming from the A horizon, thus making the B deeper and more pronounced.

In general the depth of the B horizon in the loams varies from 30 to 50 cm. or from 12 to 20 inches.

Other factors enter into the process of "growth" of the B horizon. Mechanical composition will in a way modify its depth. The coarser the material, the deeper a B horizon one might expect. A case in order is the Lakewood soil, a mature podzol. The immature Sassafras sand also shows a deep B horizon.

AGROLOGICAL ATTRIBUTES OF THE PROFILE CONSTITUTION

The profile constitution is the all-important factor in evaluating the fertility make-up of the soil. The depth of the A horizon determines, in a large measure, the "feeding area" of the plants. It is within this horizon that by and large the roots of the plant cover are located. This has been noticed in all the virgin profiles examined as well as in cultivated soils. But the A horizon by itself without favorable conditions for root distribution through the underlying B horizon is not adequate to insure a full utilization of the fertility resources of the soil. Even a depth of 9 to 14 inches—the average depth of the A horizon of the loams under consideration—is, because of the surface position of the horizon, not sufficient to meet the adverse conditions of droughts and other situations that affect the activities of the roots.

In a number of soils examined a profuse root development was noted in the B horizon, some roots penetrating into the C horizon. It is in the B horizon that the eluviated materials accumulate either permanently or temporarily.

The B horizon is from the agrologic point of view an important factor in the distribution of roots and is therefore to be reckoned with in any system of agriculture. A clear case of the relation of the B horizon to root distribution is the shallow rooting of fruit trees on some soils of New Jersey.

The compactness of the B horizon and its structure are morphological attributes which offer an explanation of the behavior of the roots in the soil. The attributes, especially the structure, are in the final analysis controlled by the pH, which as a rule is somewhat higher in the B than in the overlying A_2 horizon. Tables 1–5 show this to be the case. Wherever the pH is appreciably higher in the B horizon, the structure is as a rule more open, the consistency is more friable, and the roots extensively distributed through this horizon penetrate even into the C horizon. Such a condition prevails in the Dutchess, Dover, and Hagerstown soil series. On the other hand, in the Sassafras, Collington, Penn, and Chester the B horizon is of a lumpy, cloddy structure, of a tenacious, tough, and sometimes plastic consistency. In the Lakewood sand the presence of iron incrustations—ortsand and ortstein-like formations—was noted; not any of these incrustations are conducive to root penetration. Any attempt to get roots established in such soils means treating the B horizon.[4]

The eluviated materials from the A horizon are, as has been pointed out, caught in the B horizon. The high colloid content of this horizon is well known. Its high electrolyte content may easily be demonstrated by a conductivity test. But not until the physical condition and the reaction of this horizon have been adjusted will these electrolytes become available and the colloids function with their exchange reactions to the benefit of the plants.

A poor structure of the B horizon prevents the efficient penetration of the rain water through it and into the subsoil.[5] It is probable that the poor permeability of the B horizon may at times, during dry periods, cause the accumulaton of toxic substance and induce, during wet periods, reduction reactions.

All of the points raised simply emphasize the importance of the B horizon in agrologic practices.

EROSION AND DEPTH OF PROFILE

In some sections of the Penn series of soils the normal erosion which takes place in all soils prevents the building up of a profile. The variability in the resistance of the shale or sandstone to weathering has produced in places a shallow mantle rock cover, and under such conditions the profile is very young with only slight differentiation into horizons. Such areas are frequently mistaken for erosion areas. On soils which have a normal profile the erosion stage and degree of erosion may be determined with a high degree of accuracy.

The method of determining the erosion consists of measuring the depth of

[4] Experimental work in this direction is now in progress at the New Jersey station.

[5] By the term "subsoil" we mean the depth below the soil body, in other words, a few inches below the B horizon.

the profile, especially of the A horizon, in a protected area, wooded or in natural sod, and comparing the depth of the A in the neighboring erosion area. As a rule the gully erosion after sweeping away the A horizon cuts into the B horizon, which resists the forces of erosion because of its compactness and frequent cementation. In such a case the depth of the B horizon is helpful. In sheet erosion, however, the depth of the A horizon only is an accurate measure of the erosion stage.

CHEMICAL FEATURES OF SOIL PROFILES

The morphological features of the soils in the podzol zone, except mature podzols, do not express the degree of podzolization. To determine it accurately one must resort to chemical data.

Of the soils under consideration the Lakewood sand (table 5) has the clear-cut morphology of a mature podzol. The others are podzolic in nature, and the degree of podzolization is to be inferred from the chemical data presented.

Silica

A comparison of the distribution of SiO_2 in the profiles of the various loams shows that the soils on the Coastal Plain (table 1) are more mature than those of the Appalachian area (table 2). This is especially marked in the A_2 horizon. Both the Sassafras and the Collington loams show the highest SiO_2 content in the A_2 horizon, whereas in the same horizon of the Washington, Dover, and Dutchess this phenomenon is not so well defined.

The B horizon invariably shows a relative decrease of SiO_2 due to its enrichment with colloidal particles of the R_2O_3, Mn, and other constituents. The higher the degree of podzolization, the greater is the relative decrease of SiO_2 in the B horizon.

If a comparison is made between the Collington and Sassafras soils on the basis of the SiO_2 in the profile it becomes apparent that in the B horizon of the Sassafras the relative decrease of SiO_2 is not so marked as in the B of the Collington. The same thing is true in a comparison between the Sassafras and the Lakewood sand (table 5). This indicates a slower podzolization of the Sassafras in comparison with the Collington and the Lakewood. The reason for the impeded podzolization is the higher Ca content in the Sassafras. This phase of the problem was discussed elsewhere (5, 6). The lower Ca content in the Sassafras, as compared with the Collington, is also evident from the analytical data presented by Marbut (14).

Another probable explanation for the more rapid podzolization of the Collingon may be found in the type of parent material on which these soils formed. It is greensand marls, many of which, as is well known, decompose easily. The soil formers attack such materials and translocate the split products of the reaction at a greater rate than the feldspathic materials which comprise the larger portion of the Coastal Plain deposits.

Of the two gravelly loams reported in table 3, the Chester shows a definite

decrease of SiO_2 in the B horizon and an increase in A_1 and A_2. This feature is not expressed so prominently in the Gloucester, indicating a lower degree of podzolization. Again, as in the comparison between the Sassafras and the Collington, it is to be noted that the Ca content is higher in the Gloucester than in the Chester.

Of the two silt loams reported in table 4, the Hagerstown, even though its parent material is of limestone origin, is clearly a more mature soil than the Penn silt loam. The SiO_2 in the B horizon especially the B_2, is very low as compared with the A horizon, indicating podzolization effects. Its high pH is undoubtedly due to the additions of lime (it is to be remembered that the samples of the Hagerstown were taken from a cultivated field).

The Penn silt loam, which shows no translocation of constituents in the profile, maintains a practically uniform distribution of SiO_2. This soil, in the nomenclature of Glinka, is endodynamomorphic [see "Pedology" (9) for a discussion of this] or lithogenic, which means that the parent material determines the profile features.

A word of caution about using unconditionally the SiO_2 data as criteria of the degree of podzolization. It is to be remembered that most of these soils contain quartz silica, which obscures the significance of the SiO_2 split off from the silicates. Criteria other than SiO_2 are therefore used in substantiating deductions made about the degree of podzolization.

Iron and Aluminum

None of the chemical constituents of the soil are more indicative of the degree of podzolization than is the R_2O_3. Very little of the Fe and still less of the Al circulates in the profile through the medium of plant growth. A large share of the R_2O_3 released from the A horizon precipitates in the B horizon, and very little, if any, returns by capillary to the A horizon.

An examination of the Fe and Al data in table 1 reveals a higher accumulation of these elements in the B horizon of the Collington profile than in that of the Sassafras. This substantiates the inference, in the discussion of the SiO_2 data, that the Collington is more mature and in a higher state of podzolization than the Sassafras.

A similar condition may be noted in the light soils of the Coastal Plain (table 5). The Sassafras sand shows a relatively lower accumulation of R_2O_3 in the B horizon than does the Lakewood. The glei podzolic soil shows a high accumulation of Fe for the reason that in the gleiing process, a detailed discusson of which is to be found elsewhere (11), the soluble ferrous compounds move from the ground waters to the B and G horizons.

The data on the R_2O_3 of the loams in the Appalachian area (table 2) corroborate the inference, in the discussion on the profile depth, that because of the topography these soils are young. There is some accumulation of Fe and Al in the B horizon, but it is not so well marked as in the Coastal Plain soils. It is of interest that as far as the R_2O_3 data are concerned the Dutchess shows

the highest degree of podzolization when compared with the other two loams. This is true in spite of the higher Ca content of the Dutchess, an attribute which, as a rule, hinders podzolization. The pH data for these soils show that the Dover loam is more alkaline in spite of the low Ca content. If data were available on the exchangeable Ca, the apparent contradiction might be explained. The Dover loam probably has a higher exchangeable Ca content than the Dutchess.

The data on the R_2O_3 of the gravelly loams (table 3) corroborate the statement, made in discussing the data on the SiO_2 content in the profile of these soils, that the Chester gravelly loam is podzolized more thoroughly than the Gloucester.

The fact that the Fe, Al, and other constituents show very small differentials in the profile of the Penn silt loam (table 4) indicates no movement of them in the profile. And yet the B horizon is in its physical appearance typical of an illuviation horizon: it has a compact constitution. This simply means that the more highly dispersed particles are a resultant of physical disintegration with no change in composition.

There is definite accumulation of Fe in the B and G horizons of the glei podzolic soils; this is typical for the gleiing process, as has been pointed out elsewhere (7).

Calcium and Magnesium

There is a general tendency in the soils under consideration (and this is true for all soils in the podzol zone) to accumulate Ca in the A_0 layer. The reason for it is obvious. The high exchange capacity of the organic matter of the A_0 layer takes in the Ca released from the fresh organic matter which is constantly deposited on the surface of the soil. The same thing does not hold true for the Mg, because less Mg goes into circulation through the plant medium.

The data of the soils under consideration show that there is an accumulation of Ca, and even more of Mg, in the B horizon. That the Ca accumulation is not so well marked simply indicates that these soils, except the Lakewood (table 5), are podzolic in nature but are not mature podzols.

The case of Mg deserves special consideration,[6] inasmuch as a large portion of it released from the A horizon becomes fixed in the B horizon. In all probability the Mg ion forms with the amorphous silica secondary silicates which are more stable than the Ca-silicates. It is to be noted that in the loam soils of the Appalachian area (table 2) the accumulation of Mg in the B horizon is lower than in the loams of the Coastal Plain (table 1). This again substantiates the deductions made in the discussion on the distribution of SiO_2 and

[6] More about the rôle of Mg is to be found in the discussion on liming the soils of the podzol zone.

R_2O_3 in the profile and on the differential degree of podzolization of the soils of these two areas. Those of the Coastal Plain are of a higher degree of podzolization. The Mg data on the gravelly loams (table 3) again show that the Chester is more podzolized than the Gloucester.

The Ca and Mg data on the Penn silt loam (table 4) illustrate the lithogenic nature of this soil. The climatogenic forces are not strong enough to overcome the lithogenic character of this soil whereby the Ca and Mg distribution is displaced from the normal position in the podzol zone.

An anomalous phenomenon of accumulation of Ca in the A horizon of the Penn soil is difficult to explain. It has been pointed out by workers of the Soil Survey that road dust affects the Ca content of the surface soil and since this sample was taken along a cement road this might account for the high Ca content of the A horizon.

There is definite accumulation of Mg in the B horizons of the Sassafras and the Lakewood sandy soils (table 5). A rather low total content of Ca in the Sassafras fine sand is not typical of this soil series. The reverse is true for the Mg content: it is high in the Sassafras fine sand, which is again not typical.

Such anomalies and discrepancies in analyses of soils emphasize the importance of using a larger number of profiles before the typical course of development of the soil, in terms of its chemical composition, can be established. The typical differences found in analyzing the data on the various constituents of the profile do, however, bring out definite trends in the development of the soils.

There is a definite accumulation of Mg in the B horizon of the Sassafras and Lakewood sandy soils (table 5). It is not so sharply expressed as in the loams for the simple reason that the total Mg in the parent material of the loams is higher.

The accumulation of Mg in the G horizon of the glei podzolic soil is typical of the gleiing process, which was discussed more fully elsewhere (7).

Manganese

The general trend of Mn movement in the podzol profile results in an accumulation of Mn in the B horizon. This tendency, with few exceptions, may be noted in most of the soils under consideration. The accumulation is not so clear-cut as in true podzols,[7] which indicates the immature state of podzolization of these soils.

A noteworthy phenomenon is the relatively high Mn content of the A_0 layer in most of these soils. The source of this Mn is unquestionably the plant tissue which is being deposited on the surface and in the A_1 horizon. It is very likely associated with the humus complexes which retain appreciable quantities of this element in exchangeable (by electrodialysis) and nonexchangeable forms.

[7] Those who are interested in the distribution of Mn in the profile of true podzols are referred to the data of Marbut (14).

Nitrogen

The A_0 layer of any soil, irrespective of the zonal type, is, because of its organic constituents, the richest in nitrogen. The type of vegetation, which varies with the zonal soil types, will in large measure determine the N content of the respective A_0 layers. Thus in the grass-land country the N content is undoubtedly higher than in the forest country. This observation was made long ago by Hilgard (3) in his classical researches on the soils of the humid and arid regions.

The data on the N content of the A_0 layer of the soils under consideration lack uniformity for the reason that the organic matter is contaminated with mineral material which clings to it. More careful sampling of the A_0 is required in order to get the fine variations which might occur in the soils as a result of microclimatic features, texture of material, local types of vegetation, and other local factors. A better understanding of the distribution of N in the profile may be gained from the analytical data on the profile below the A_0 layer.

Outside of the mature podzol—the Lakewood in table 5—there is a decrease of N with depth in the soils studied. An outstanding feature of the N data is that the loam soils of the Appalachian area (tables 2 and 3), with the exception of the Chester, contain more N than the corresponding textural type of the Coastal Plain. The reason for this may be sought in the microclimatic features of the two areas. It was pointed out earlier in this paper that the average temperature is higher in the Coastal Plain. The rainfall is also higher in the Coastal Plain. It is probable, however, that the low winter temperatures in the Appalachian area are in a large measure responsible for the higher N content in the soils of this area. Such temperature conditions keep down the activities of the soil microorganisms. The freezing is conducive to a more stabile—aging effect—condition of the organic colloids.

The two silt loams (table 4) show tendencies similar to the loams of the Appalachian area.

The N data on the Lakewood sand (table 5) show again the podzol nature of this soil, or rather its maturity. The N content of the B horizon is higher than that of the A_2. It is due, as pointed out elsewhere (11), to the movement of the organic matter as a sol and its precipitation in the B horizon. This finely dispersed organic matter is, as a rule, of a higher nitrogen content than the coarser fractions. Because of this, it is possible to have a higher organic matter content in the A_2 horizon and still have a higher N content in the B horizon. The Sassafras sand (table 5) is trailing the Lakewood sand, even though its podzolization features are not so marked as those of the Lakewood sand.

Phosphorus

The data on the distribution of P in the profile of the soils under consideration are clear-cut. The A_0 has a high P content, because of the organic phos-

phorus compounds. The A horizon shows a drop in P, indicating a release of it in the process of eluviation. In the B horizon the P content increases, indicating that the eluviated P precipitates at this point.

The movement of P in the profile of the brown forest soils is evident in every profile examined, as illustrated in tables 1–5. Both the Coastal Plain and Appalachian areas show a similar behavior. The only exception is the Penn soil of the Piedmont area. The peculiar behavior of this soil is not due to its geographic-geologic position, but to its endodynamomorphic state, as shown earlier in this paper.

Reaction

The outstanding feature of the data on the reaction of the soils, as indicated by the H_2O extract, is that those of the Coastal Plain are more acid than those of the Appalachian area. There is, however, enough replaceable hydrogen in the soil absorption complex to give most of the soils of this zone a similar pH when extracted with a neutral salt. The data on unsaturation show again that the Appalachian soils are less acid than those of the Coastal Plain.

The differences mentioned may be attributed to two factors: first, the composition of the parent material, and secondly, the microclimatic conditions. The parent material of the soils in the Appalachian area contain, as a rule, more alkaline earth bases than that of the Coastal Plain. The soils of the Appalachian area receive less precipitation than the soils of the Coastal Plain and hence suffer less leaching.

True to form the pH is, as a rule, lowest in the A_2 where the most destructive activity of the podzolization process takes place. The pH rises again in the B horizon and drops or rises, depending on the parent material, again in the C horizon. This tendency is to be noted in all soils of the podzol zone, and the soils under consideration are no exception.

The high pH of some of the A_0 layers is to be attributed to the temporary presence of bases released from freshly deposited dead organic matter. In some instances, as has been frequently demonstrated by the author, ammonia is found in the processes of decomposition of organic matter. In general, however, such a high pH in the A_0 layer is a temporary condition.

The high pH of the Hagerstown soil (table 4) is due to the parent material—limestone—and to the addition of lime to the surface soil which is under cultivation.

Cation exchange

The cation exchange capacity in the A_0 layer is the highest of any part of the profile. This is due to the organic matter which has a very high cation exchange capacity. It drops sharply in the A_1 horizon (the drop depending on the organic matter content in this horizon); still more in the A_2 horizon, especially in the mature podzols, as in the Lakewood soil (table 5); rises again in the B horizon; and usually drops (depending on the parent material) in

the C. The graph of the exchange capacity, if such should be constructed, of the soils in the podzol zone has the same curvature as that of the pH of these soils. This may easily be noted from the data on the soils analyzed.

There is no zonal soil, except the laterites, in which there should be such a wide difference between the exchange capacity of the A_0 and the underlying horizons as in the podzols.

A comparison of the exchange capacity of the loam soils in the Coastal Plain (table 1) and of the loams of the Appalachian area (table 2) shows that the latter have a higher capacity. If we recall the N data, the soils of the Appalachian area have a higher N content, which means a higher organic matter content and hence a higher cation exchange capacity.

SOME AGROLOGICAL INFERENCES FROM CHEMICAL DATA OF PROFILES

The fertilizer practices in the podzol zone should be guided by the consideration of opposing the destructive tendencies of the podzolization process. Since acid hydrolysis is the chief driving force of podzolization, the soils of the podzol zone should be treated in such way as to minimize such a hydrolysis and thereby preserve the valuable potassium and alkaline earths in the colloidal complex and prevent its disruption.

One of the effective means of reducing the hydrolytic effects mentioned is the reduction of the unsaturation of the complex. Empirically this had been done for more than 50 years by the methods of liming the soil. With a knowledge of the chemistry of the soil profile a more rational and more refined method of liming may be introduced. From the data presented on the distribution of Ca and Mg, the exchange capacity, and the unsaturation of the soil profile of the Coastal Plain, it is clear that an application of lime deeper in the profile would greatly benefit these soils. No such practice is called for by the soils of the Appalachian area, which have a higher exchange capacity and a lower unsaturation than the Coastal Plain soils.

The retention of the Ca ion in the soils of the podzol zone is of primary importance. It is this ion which is most efficient in opposing podzolization. In applying fertilizers, the preservation of this ion should be kept in mind. In choosing NH_4 salts the sulfate or phosphate should, in many instances, be preferred to the chloride or nitrate. In the case of the K salts, again, the sulfates should be given preference. The phosphates and sulfates of Ca are insoluble, the latter less so than the former but still insoluble enough not to be leached out immediately. A practice of this kind undoubtedly would greatly benefit the soils of the Coastal Plain area.

The fixation of Mg in the B horizon, through the formation of Mg-silicates which are more stabile than the Ca-silicates and of "new formations" like polygorskite—a Mg-Al-silicate, prompt a new orientation as to the type of lime one should use.

In recent years the Mg problem has been studied empirically, and the bene-

ficial effects of the Mg have been demonstrated. And, as in the case of the Ca, the knowledge of the distribution of Mg in the profile may elucidate and rationalize the proper use of liming materials which carry magnesium.

There is another angle to the Mg problem. Since the Mg becomes fixed in the B horizon, there is the danger of too wide a ratio of Ca to Mg for optimum conditions of plant growth. Ever since the classical work of Loew (13) on the importance of the Ca:Mg ratio in the metabolism of plants there has been no agreement on the importance of this ratio in the soil. The conflicting reports may in a large measure be attributed to the differences in the distribution of the Mg in the profile and to the lack of knowledge, until recently, about the rôle of the Ca and Mg in the exchange complex. The latter point was elucidated by Gedroiz (2), who demonstrated the relation of the Ca:Mg ratio in the soil absorption complex to the efficient utilization of these ions by plants.

The lower fixation of Mg in the B horizon of the soils in the Appalachian area, as compared with the soils of the Coastal Plain, which is an index of the lower degree of podzolization of the Appalachian soils, indicates a greater mobility of this ion. Because of this factor, together with the high exchange capacity of these soils, they are not likely to be so easily unbalanced, with respect to the Ca:Mg ratio, as the soils of the Coastal Plain.

Without a knowledge of the distribution of the Mg in the profile and its resources in the exchange complex, the use of Mg-lime may enhance too narrow a ratio of Ca to Mg which, as pointed out elsewhere (8), is just as harmful as too wide a ratio.

With the fertilizer practices in the podzol zone large quantities of acid phosphate are used. These add Ca as the phosphate and large quantities of $CaSO_4 \cdot 2H_2O$. The use of Mg-lime from time to time will offset the wide Ca:Mg ratio created by the Ca from the acid phosphate.

In recent years a new acid phosphate has been introduced, namely, Mg-acid phosphate. It is produced by the action of H_3PO_4 on Mg-silicates. It is claimed that this new source of phosphorus is superior to Ca-acid phosphate. Its tri and divalent salts are more soluble than the corresponding Ca salts. The presence of silicic acid is conducive to a more efficient utilization of the phosphorus. As a carrier of Mg this phosphate may help to balance the Ca:Mg ratio. Experimental evidence on the efficiency of this P carrier was presented by Druzhinin (1).

Of the three so-called deficient plant foods added as fertilizers, N—P—K, the P is frequently of much concern to the student of soil fertility. Soluble phosphates added to the soil soon become insoluble or, as the term goes, they "revert." There is a general notion that soluble phosphates are fixed in all soils at the point, or in the immediate vicinity, of their placement. The P is spoken of as one of the fertilizer constituents which does not move.

From the data presented in tables 1–5 on the distribution of P in the profile it is evident that there is no justification for this generalization with reference to the soils in the podzol zone. There is definite translocation and movement

of P, and, although the bulk of the applied P is fixed in the cultivated layer (A_p), some of it undoubtedly moves to the underlying horizons.

In considering the mobility of P in the profile it is well to remember that in the equilibrium conditions of a solid-liquid system it is not always the most insoluble salt that is precipitated first. The precipitation depends on the relative concentration values of the ions which determine the equilibrium. Thus if we have an appreciable concentration of silicic acid, as we do in the podzol zone, the more soluble Ca-silicate will form instead of the Ca-phosphate from the slightly dissociated $Ca_3(PO_4)_2$. This might explain why the introduction of silicates is frequently conducive to the more efficient utilization of the phosphates.

SUMMARY

The geographic-geologic features, the topography, and the climate of a number of soil profiles in New Jersey are presented.

The variations in the depth of the profiles and the constitution of 13 soils are analyzed pedologically, and the agrological inferences are discussed.

The relation of the erosion problem to the profile constitution is noted.

Chemical analyses of 13 soil profiles are presented and discussed in the light of the processes involved in the formation of these profiles.

Some agrological aspects of the profile studies, with special reference to Ca, Mg, and P, are presented.

REFERENCES

(1) DRUZHININ, D. V. 1936 A new phosphate fertilizer. *Khimizatziya Sotzialist. Zeml.* No. 2–3: 59–63.

(2) GEDROIZ, K. K. 1931 The exchangeable cations of the soil and the plants: II. Liming and the quantity of exchangeable Ca and Mg in soils. *Udobrenie i Urozhai* No. 3: 149–163.

(3) HILGARD, E. W. 1906 Soils. Macmillan Co., New York.

(4) JOFFE, J. S. 1932 Soil profile studies: IV. Morphological and chemical evidence of podzolization. *Soil Sci.* 33: 217–237.

(5) JOFFE, J. S. 1933 Genesis of podzols [Russian]. *Pochvoved.* 28: 374–381.

(6) JOFFE, J. S. 1933 Morphology and genesis of podzols. *Amer. Soil Survey Assoc. Bul.* 14: 22–29.

(7) JOFFE, J. S. 1935 Soil profile studies: VII. The glei process. *Soil Sci.* 39: 391–401.

(8) JOFFE, J. S. 1936 The availability of replaceable cations of the soil to plants [Russian]. *Khimizatziya Sotzialist. Zeml.*, No. 5: 50–59. [See also a resumé of this paper in *Trans. Third Internatl. Cong. Soil Sci.* (1935) 1: 66–67.]

(9) JOFFE, J. S. 1936 Pedology. Rutgers University Press, New Brunswick, N. J.

(10) JOFFE, J. S., AND LEE, L. L. 1929 Soil profile studies: II. Methods used in the profile survey of New Jersey soils. *Soil Sci.* 28: 469–479.

(11) JOFFE, J. S., AND WATSON, C. W. 1933 Soil profile studies: V. Mature podzols. *Soil Sci.* 35: 313–331.

(12) LEWIS, J. VOLNEY, AND KÜMMEL, H. B. 1915 The geology of New Jersey. Geol. Survey of N. J. Bul. 14.

(13) LOEW, O. 1903 The physiological rôle of mineral nutrients in plants. U. S. Dept. Agr. Bur. Plant Indus., Bul. 45.

(14) MARBUT, C. F. 1935 The Soils of the United States. *Atlas of American Agriculculture*, pt. III. U. S. Dept. Agr., Bur. Chem. and Soils.

THE VARIETY OF SOLONETZ RED SOILS IN THE VICINITY OF THE VILLAGE OF MARCOPOULO, ATTICA

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The wide-spread distribution of red soils in Attica offers almost limitless possibilities for investigation and for classification of their characteristics in accordance with the factors of soil formation.

In an earlier paper (3), the authors described the process of soil formation in those red soils of Attica that normally overlie limestone in the absence of the influence of ground waters and of pronounced erosion.

In this article, we shall examine the properties of a $CaCO_3$-free soil with a very decided red color but different from those soils discussed in the previous work. This red soil, covering a considerable area in the vicinity of Marcopoulo, along the Athens-Laurion Road, is found in the following environment:

The broad valley near Marcopoulo is surrounded by rather low and much-eroded mountains, composed of limestone and other rocks. It is generally of a smooth saucer-shaped topography, slightly undulating because of the denudation processes. In this valley one sometimes meets the remnants of erosion in the form of individual hillocks. At the foot of the hills, remains of river terraces are still noticeable, although strongly inundated.

The red soils covering this valley attain their greatest depth and intensity of color in the vicinity of Marcopoulo. Close to the village of Liopessi and the Bay of Vraonas, both the depth and the intensity of color diminish. The profile taken 1.5 km. N.-N.W. of Marcopoulo, almost in the center of the red soil area, has the following characteristics:

Horizon $A_1 + A_2$, 0–12 cm. Of brick-red color, sandy, weakly coherent, structureless, with a tendency to slake when wetted, and, upon drying, to form clumps which may be easily crushed between the fingers. Thickly interwoven with roots. There is an admixture of skeletal pieces in the form of rounded reddish quartz, and on the surface one may find, here and there, slightly rounded pieces of limestone. No effervescence with HCl.

Horizon B, 12–42 cm. Dark red, very compact, with cracks which form irregular, sharp-angled, columnar pieces. The sides of the cracks are of a darker color, shading into brown. On the angles of the pieces are remnants of dead roots. Red colored quartz gravel is found in very small quantities. No fragments of limestone. No effervescence with HCl.

Horizon B_1, 42–71 cm. Dark red with brownish tinge, darker than horizon B. Very compact. Broken by cracks into large prismatic clods with shiny surfaces. The sides of the cracks are of a still darker color. On the angles of the clod, one finds dark brown spots as well as remnants of dead roots. No gravel. No effervescence with HCl.

Horizon C, 71–95 cm. Bright bordeaux red, very compact, of cemented conglomerate containing fragments of weathered limestone. The compactness of the horizon is so great that it resists the force of instruments; the limestones are of various sizes, sometimes reaching the dimension of a man's fist. Strong effervescence with HCl.

In the quarries situated in the lower part of the topographical relief, close to the profile described, where red clay is dug for various purposes, at a depth of 75 cm. one can see in the carbonate-free horizon B_1, many black spots, smears, and occasional small iron-manganese concretions. The last of these have been described by Zvorykin (9) for red soils influenced by ground waters. We also find here traces of gleiing of the soil, in the form of light gray veins and spots frequently encountered on the dark red background. From these facts it is evident that the ground waters formerly rose closer to the surface and left in the profile definite effects.

The veins of limestone fragments in horizon C, mainly composed of carbonate-free red clay, as well as the fragments of limestone found on the surface of the soil, indicate the heterogeneous nature of the sediment. Because of the character of the surrounding mountains, consisting, as they do, of limestone and other rocks, such a heterogeneity is not surprising. Since the profile under consideration, however, has well-developed genetic horizons and not layers formed mechanically by the denudation processes (a phenomenon often observed on the broken topography of Greece), it is to be presumed that these soils have had in the past a very long period of development without any influence of erosion.

The laboratory investigation of the soils has shown the following facts.

RESULTS OF CHEMICAL ANALYSIS

The results of chemical analysis of the soil passing through a 2-mm. sieve are given in tables 1 and 2. The results in table 2 are calculated on mineral content minus humus and CO_2 content.

From table 1 it is apparent that the hygroscopic moisture increases with the depth, as does the loss on ignition. This latter fact shows the increase, in general, of organic matter in the lower horizons which corresponds to the color darkening.

The carbonates occur exclusively in horizon C in the form of veins in the mass of red clay.

SiO_2 and R_2O_3 behave as in podzolic soils, the former decreasing sharply with depth, and the latter accumulating in the lower horizons. This accumulation is clearly brought out in table 2, especially for Al_2O_3.

The MnO is irregularly distributed; in horizons B and C its content is generally very high especially when compared with that of horizons $A_1 + A_2$ and B_1. If we accept the postulate of Vernadsky (8) that the presence of large quantities of Mn in the soil is due to biological processes, then we have evidence, on the one hand, of the ancient origin of this soil and, on the other hand,

of the influence of ground waters on the soil-forming processes, the latter of which has also been pointed out by Zvorykin (9).

CaO is fairly uniformly distributed in carbonate-free horizons of the soil, and increases sharply in horizon C, which, of course, is quite obvious from the description of the profile. The quantity of MgO continuously increases with the depth. K_2O and Na_2O behave similarly.

The $\frac{SiO_2}{Al_2O_3}$ and $\frac{SiO_2}{R_2O_3}$ molar ratios decrease with depth, which indicates the increase of the allitic part (5). Thus, if we base our conclusions only on the total analysis, we must assume that, under the climatic conditions of Attica,

TABLE 1

Chemical analysis of the soil < 2 mm.

HORIZON	DEPTH	H_2O AT 105°	LOSS ON IGNITION	CO_2	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	TOTAL
	cm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
$A_1 + A_2$	0–12	2.46	3.89	0	75.54	9.23	5.49	0.08	1.32	0.56	1.08	3.07	100.26
B	12–42	5.32	3.47	0	68.15	15.53	5.67	0.32	1.13	0.91	1.72	2.88	99.78
B_1	42–71	7.36	5.39	0	58.25	21.85	5.91	0.07	0.95	1.13	2.31	3.84	99.80
C	71–95	7.58	6.59	6.81	43.13	19.65	8.16	0.18	7.77	1.58	2.47	3.72	100.06

TABLE 2

Chemical analysis of the soil < 2 mm. calculated on mineral content minus humus and CO_2

HORIZON	DEPTH	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	$\frac{SiO_2}{Al_2O_3}$	$\frac{SiO_2}{R_2O_3}$
	cm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		
$A_1 + A_2$	0–12	78.59	9.61	5.72	0.08	1.37	0.58	1.12	3.19	13.90	10.09
B	12–42	70.60	16.09	5.87	0.33	1.40	0.94	1.78	2.98	7.47	6.06
B_1	42–71	61.34	23.01	6.23	0.07	1.02	1.19	2.43	4.04	4.53	3.87
C	71–95	46.39	22.44	9.32	0.21	8.87	1.80	3.47	4.25	3.51	2.77

at a 60-m. level very considerably podzolized red soils can be found. Such a conclusion is also confirmed by the distribution of clay $< 2\,\mu$ (table 3), with its highest content in horizon B_1 and its lowest in $A_1 + A_2$, a typical distribution for a strongly podzolized profile. We shall see presently whether this type of soil is really podzolized.

In view of the great interest in the soil under examination, we also made a total analysis of the clay fraction $< 2\,\mu$ of all horizons of the profile (tables 4 and 5).

These tables show at first glance an extreme constancy in the clay composition of the various genetic horizons. A more or less distinct difference is formed in the loss on ignition, which increases with depth. This fact may

serve as a proof that the most dispersed portion of organic matter is found in the upper horizons of the profile. This is also apparent from a comparison of tables 1 and 4.

CO_2 is found only in the carbonate vein of horizon C, where it occurs in considerably larger quantities than in the entire profile (table 1). This result proves that the main mass of $CaCO_3$ is located in the larger fractions above 2 μ.

TABLE 3

Clay content of the soil

HORIZON	DEPTH	CLAY < 2μ
	cm.	*per cent*
$A_1 + A_2$	0–12	19.97
B	12–42	40.24
B_1	42–71	56.32
C	71–95	46.48

TABLE 4

Chemical analysis of the clay fraction < 2μ

HORIZON	DEPTH	H_2O AT 105°	LOSS ON IGNITION	CO_2	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	TOTAL
	cm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
$A_1 + A_2$	0–12	6.70	11.09	0	43.02	26.62	11.22	0.18	2.39	1.81	2.58	1.03	99.24
B	12–42	7.22	9.55	0	43.84	25.90	11.54	0.42	1.71	2.25	2.45	1.49	99.14
B_1	42–71	6.99	8.95	0	43.58	27.91	10.57	0.20	1.39	1.77	2.68	1.71	98.76
C	71–95	6.16	6.96	0.98	44.20	28.79	10.89	0.33	2.70	2.23	2.99	0.71	99.78

TABLE 5

Chemical analysis of the clay fraction < 2μ calculated on mineral content minus humus and CO_2

HORIZON	DEPTH	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	$\frac{SiO_2}{Al_2O_3}$	$\frac{SiO_2}{R_2O_3}$
	cm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		
$A_1 + A_2$	0–12	48.83	30.45	12.74	0.20	2.71	2.05	2.93	1.17	2.72	2.15
B	12–42	47.37	28.64	12.76	0.47	1.89	2.49	2.71	1.64	2.81	2.18
B_1	42–71	47.87	30.66	11.61	0.21	1.52	1.94	2.94	1.87	2.64	2.14
C	71–95	47.97	31.27	11.83	0.36	2.93	2.42	3.28	0.77	2.60	2.24

Thus only a small quantity of the carbonates goes into dispersion, which is also ascertained by the abrupt reduction of the total quantity of CO_2 in the clay of horizon C in comparison with the total soil.

Apparently under the conditions of the process of weathering which takes place in the profile, calcium carbonate is removed first of all, and only the larger fractions are retained in the soil.

Among the alkalies and alkaline earth bases, MgO shows the greatest increase through all horizons; on the other hand, Na_2O shows the greatest loss. The results given seem to confirm the opinion of Polynov (5) about the phases of weathering.

The SiO_2 in the clay of all horizons decreases and the R_2O_3 increases when compared with the total soil. There is a tendency toward a slight increase of Fe_2O_3 in the clay of horizons $A_1 + A_2$ and B in comparison with B_1 and C.

The ratios of $\frac{SiO_2}{Al_2O_3}$ and $\frac{SiO_2}{R_2O_3}$ in the clay show that the soil upon weathering attains a more allitic character, i.e., the process of soil formation tends toward laterization (6). The tendency toward this process in the whole profile is confirmed by the extraordinary stability of composition of the clay of the eluvial and illuvial horizons.

TABLE 6

*Exchangeable bases**

HORIZON	DEPTH	Ca	Mg	K	Na	Ca	Mg	K	Na	TOTAL EXCHANGEABLE CATIONS	Na IN TOTAL QUANTITY OF EXCHANGEABLE CATIONS
	cm.	*per cent*	*per cent*	*per cent*	*per cent*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*per cent*
$A_1 + A_2$	0–12	0.448	0.054	0.055	0.078	22.40	4.50	1.39	3.38	32.67	10.35
B	12–42	0.460	0.087	0.058	0.136	23.00	7.24	1.47	5.91	32.71	18.07
B_1	42–71	0.630	0.098	0.047	0.124	31.50	8.17	1.19	5.38	46.24	11.63
C	71–95	0.390	0.348	0.057	0.120	19.50	29.00	1.43	5.21	55.14	9.46

* After Gedroiz's method with $BaCl_2$. No traces of H have been noticed by the authors.

In the morphological description, we have pointed out the difference in the coloring of individual horizons of the profile; on the basis of analytical material, we can now state definitely that the intensity and the color are related to the quantities of clay enriched with Fe_2O_3.

QUANTITATIVE DETERMINATION OF EXCHANGEABLES CATIONS

The soil under examination shows a considerable difference with respect to the quantity of exchangeables cations in the various genetic horizons: the quantity increases with depth.

Exchangeable Ca predominates in all horizons except C. In horizon C there is a large absolute quantity of absorbed Mg. It should be noted that the quantity of absorbed Mg in the other horizons also is relatively very large; this fact is, in our opinion, associated with the relative increases of MgO in the clay fraction, in comparison with its content in the total soil. Such a fact indicates a high degree of rock weathering or a highly advanced process of soil formation, which is in line with the elucidation of this phenomenon by Polynov

(5) and is corroborated by the increase in the allitic properties of the clay fraction noted by the authors.

For the soil under examination, however, the highly advanced process of soil formation may be caused not only by its ancient origin, but also by the action of absorbed Na. From table 6 we see that the given profile possesses strongly solonetzic characteristics. With the exception of horizon $A_1 + A_2$, the absorbed Na content exceeds 4.5 m.e.; the percentage of Na in the total absorbed cations is high throughout. Orlovsky (4) points out that strongly solonetzic characteristics appear at a 4.5 m.e. content of absorbed Na and, furthermore, that the most unfavorable structure of the soil is manifested at a

TABLE 7

*Water extract of the soil**

HORIZON	DEPTH	TOTAL ALKALINITY IN H_2CO_3	Cl	SO_3
	cm.	*m.e.*	*m.e.*	*m.e.*
$A_1 + A_2$	0–12	0.40	0.34	0.20
B	12–42	0.31	0.37	0.32
B_1	42–71	0.26	0.37	0.14
C	71–95	0.57	0.46	0.35

* Insignificant traces of Na_2CO_3 are found in horizons $A_1 + A_2$ and C.

TABLE 8

SiO_2 and Al_2O_3 extracted with 5 per cent KOH

HORIZON	DEPTH	SiO_2	Al_2O_3	$2SiO_2Al_2O_3$	RESIDUE		$\frac{SiO_2}{Al_2O_3}$
					SiO_2	Al_2O_3	
	cm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	
$A_1 + A_2$	0–12	1.036	0.740	1.152	0.462	0	2.38
B	12–42	1.316	1.112	2.419	0.072	0	2.08
B_1	42–71	1.576	1.052	2.342	0.337	0	2.54
C	71–95	1.556	1.068	2.314	0.335	0	2.52

15 per cent content. Sushko (7) mentions that the accumulation of absorbed Mg in a number of horizons of solonetzic soils is indicative of the solodization process, i.e., a process which favors the rapid destruction of silicates and allumino-silicates, as stated by Gedroiz (1).

RESULTS OF ANALYSES OF WATER EXTRACTS

The results of analyses of water extracts show that the soils contain small quantities of chlorides and sulfates (table 7). Traces of sodium carbonate are found in horizons $A_1 + A_2$ and C and of sodium bicarbonate in the other horizons. It may be assumed that formerly, when the water table was high, the content of water-soluble salts was higher.

5 PER CENT KOH EXTRACT

Table 8, containing the results of the treatment of soil with 5 per cent KOH, shows that comparatively little SiO_2 is extracted; neither is the combined $2SiO_2\ Al_2O_3$ high, and therefore the $\frac{SiO_2}{Al_2O_3}$ is low. This phenomenon occurs in spite of the appreciable content of absorbed Na in the soil. Apparently the process of solodization in this soil has not progressed very far.

It is very probable that this condition occurs because, in the process of weathering, the soil accumulates Al_2O_3 and assumes a more allitic character; there is considerable saturation of the soil with calcium and magnesium, which exert a protective effect on the soil colloids. Both calcium and magnesium are mentioned in view of the findings of Sushko (7), who showed that Mg saturation does not increase the dispersion of the soil and in reality is nearer in its effect to Ca than to the monovalent cations, K and Na.

CONCLUSIONS

From observations in the field and from laboratory investigations the following conclusions may be drawn:

In the vicinity of the village of Marcopoulo there is a solonetzic $CaCO_3$-free red soil of very ancient origin, in which the soil-forming process is directed toward laterization, as is indicated by the total analyses of the soil and the clay. The soil-forming process here is complicated by the influence of absorbed Na.

The solonetzic properties of the soil are apparent from the morphologic study of the profile and are strongly marked in the structure of horizons B and B_1. Horizon $A_1 + A_2$ is also very typical of a solonetzic soil, being considerably bleached and impoverished of the clay fractions when compared with the underlying horizons.

The dark spots and smears, as well as the occasional small dark concretions and the light gray veins, prove the influence of the ground waters on the process of soil formation. The existence of this influence is confirmed by the considerable quantities of absorbed Na, as well as by the presence of chlorides and sulfates, found in the water extract. Thus this is an example of "underground" salinization of red soil (5).

The process of natural desalinization has progressed appreciably, and apparently this is a case of solonetz solodization (1). This is, therefore, a relic formation.

From what has been said, it is apparent that this soil-forming process in Attica is very complex, and, therefore, for a rational agriculture, the division of the country into definite zones is of practical importance.

REFERENCES

(1) GEDROIZ, K. K. 1926 Solodi. Bul. Nosovsk. Opytn. Stan. 44]Russian[.

(2) HARASSOWITZ, H. 1926 Studien über mittel- und süderopäische Verwitterung. *Geol. Rundschau.* 17 A: 200.

(3) NEVROS, K. I., AND ZVORYKIN, I. A. 1936 Investigations of red soils of Attica, Greece. *Soil Sci.* 41: 397–415.

(4) ORLOVSKY, N. V. 1934 Engineering estimation and chemical reclamation of solonetzic soil in Kazakstan. *Pochvoved.* No. 3: 340–361 [Russian].

(5) POLYNOV, B. B. 1934 Écorce de décomposition. *Acad. Sci. U. S. S. R. Leningrad Pub.*, pp. 148, 149–150, 162–164, 166–168 [Russian].

(6) ROBINSON, G. W. 1932 Soils, Their Origin, Constitution and Classification, pp. 93–94, 205, 271, 288. London.

(7) SUSCHKO, S. J. 1933 Die Rolle des adsorptiv gebundenen Magnius bei der Entwicklung der solonetzartigen (Alkalienboden) Eigenschaften. *Khim. Sotz. Zeml.* No. 3: 217–220.

(8) VERNADSKY, V. 1924 La Géochimie, pp. 74–100. Paris.

(9) ZVORYKIN, I. A. 1934 Sur les concrétions ferriques de quelques terres rouges de la Grèce. *Bul. Czechoslov. Acad. Agr.* 10: 11–14.

IONIC RELATIONSHIPS IN PEAT

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In a previous study dealing with the electrodialysis of peat, observations were made which seemed to indicate that certain ions were present in the diffusates in combination with organic matter. A brief report on that subject has been published from this laboratory (5). The purpose of the present paper is to discuss the matter in greater detail and to point out the probable forms of many of the constituents of peat as they exist in nature.

PEATS USED

Two virgin peats were used in the experiment. They were collected from the surface foot of woody deposits derived mainly from the remains of deciduous and coniferous vegetation. The peats were air-dried and were prepared for analysis by grinding in a Wiley mill until they would pass through a 40-mesh sieve. They differed widely in chemical composition, particularly in the amounts of ash and calcium contained. Some of the differences are recorded in table 1. Peat A, having a reaction of pH 5.7, was known to be 82 per cent saturated with bases; peat B, having a reaction of pH 3.9, was known to be 15 per cent saturated with bases. Peat A was collected from a deposit underlain with blue, sticky, calcareous clay at a depth of about 5 feet. Peat B was collected from a deposit underlain with gray non-calcareous clay at a depth of about 4 feet. It was on the basis of these several differences that the two peats were selected for study.

METHODS USED

A battery of Mattson cells was used to electrodialyze the peats. Cellophane and parchment paper were used as membranes to separate the anode and the cathode compartments, respectively, from the middle compartment. The electrodes were of platinum gauze approximately 9 by 15 cm. in size. Twenty grams of peat was electrodialyzed for 72 hours by means of a motor-generator set of 250 volts and 0.6 ampere, and with no resistance in the circuit. The current was not turned off during the period of operation. The temperature was held constant by means of glass coils through which water was running continuously.

A large amount of peat was electrodialyzed in order to obtain measurable amounts of certain of the constituents in the diffusates. Previous experiments

had shown that the peats contained large amounts of exchangeable cations and that a relatively long period of electrodialysis was necessary to bring the peats to a state of unsaturation with respect to metallic cations. Small amounts of some of the cations, however, were liberated from the peats as long as electrodialysis was continued. To facilitate the rapidity of the removal of the ions, and to lessen the amount of ionic precipitation on the cathode membrane, the solutions were removed from the outer compartments of the cell every 4 hours.

Although the results recorded in the tables of this paper are average values of duplicate determinations made simultaneously, the experiments were repeated time and again with essentially the same results.

TABLE 1

Chemical composition of the peats used in the investigation

PEAT	CONSTITUENTS IN SOIL, DRY BASIS												
	Ash	SiO_2	Fe_2O_3	Al_2O_3	MnO	CaO	MgO	Na_2O	K_2O	S	P_2O_5	N	C (Inorganic)
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
A	17.3	1.78	1.33	0.33	0.03	7.44	0.49	0.02	0.09	0.72	0.23	2.85	0.14
B	7.5	4.47	0.24	0.53	0.01	1.00	0.16	0.02	0.08	0.21	0.18	1.77	0.03

TABLE 2

Ions found in the catholyte during 72 hours of continuous electrodialysis

100 gm. of dry soil

PEAT	TREATMENT OF DIFFUSATE	ORGANIC MATTER*	Si	Fe	Al	Mn	Ca	Mg	Na	K	S	P
		mgm.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*
A	Ignited	3810	2.95	10.50	1.84	0.49	250.60	22.18	0.19	0.51	0.68	0.40
	Not ignited	....	2.91	10.50	2.13	0.20	250.80	.....	....	....	0.00	0.33
B	Ignited	1579	1.08	1.31	0.78	0.39	34.23	6.70	0.14	0.83	0.08	0.06
	Not ignited	....	0.79	1.16	0.90	0.25	34.53	....	....	....	0.00	0.06

* Loss on ignition.

IONS OF THE CATHOLYTE

The amounts of the ions found in the combined cathode fractions are recorded in table 2. Analyses were not made of the individual fractions because the order of the removal of the ions from natural peat, with reference to time, had been previously determined (4). As shown in table 2, relatively large amounts of organic matter were present in the catholyte of each of the peats. Sulfur and phosphorus, ions normally migrating to the anode, were found at the cathode. Silicon was found also at the cathode, and in larger amounts than at the anode.

An analysis of the ions of the catholyte revealed that the ions, with the exception of those of sulfur, could be completely precipitated without first

destroying the organic matter.[1] This is shown in table 2. Such a relationship suggests that few, if any, of the metallic ions were an integral part of the organic matter. On the other hand, none of the sulfur of the cathoyte could be precipitated in the presence of the organic matter. This seems to imply that the sulfur was a constitutional part of the organic matter. A test showed that sulfate ions were not present in the catholyte.

IONS OF THE ANOLYTE

The fractions from the anode compartment were combined and concentrated *in vacuo* at a temperature not exceeding 45°C. The resulting solution was highly colored, but clear, in appearance, no perceptible precipitation having occurred during the concentration process. On analysis the solution was found to contain ions which normally function as cations. As shown in table 3,

TABLE 3

Ions found in the anolyte during 72 hours of continuous electrodialysis

100 gm. of dry soil

PEAT	TREATMENT OF DIFFUSATE	ORGANIC MATTER*	Si	Fe	Al	Mn	Ca	Mg	Na	K	S	P	Cl
		mgm.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*
A	Ignited	4804	0.65	1.30	0.25	0.00	0.11	0.15	0.04	0.02	9.50	4.50	tr
	Not ignited	....	0.00	0.00	0.00	....	0.00	....	....	....	0.62	3.90	..
B	Ignited	1217	0.15	0.06	0.10	0.00	0.04	0.02	0.02	0.01	1.20	3.62	tr
	Not ignited	....	0.00	0.00	0.00	....	0.00	....	....	....	0.00	2.77	..

* Loss on ignition.

determinable amounts of iron, aluminum, calcium, magnesium, sodium, and potassium were present in the anolyte of each of the peats. These ions, as far as they could be determined, were definitely associated with the organic matter of the solution because they could not be precipitated in the presence of the organic matter.

Considerably more sulfur and phosphorus were found in the anolyte than in the catholyte. This is shown in tables 2 and 3. Practically all of the sulfur of the diffusates was in combination with organic matter in a form from which it could not be precipitated. Only a part of the phosphorus appeared to be intimately associated with organic matter; most of it could be precipitated without the destruction of the organic matter.

ELECTRODIALYSIS OF THE ANOLYTE

The anode dialyzates resulting from the electrodialysis of two distinct charges of peat were combined and concentrated *in vacuo* in the manner already

[1] The method of procedure precluded the determinations of magnesium, sodium, and potassium.

described. The concentrated solution, representing 40 gm. of soil, was electrodialyzed for 144 hours to determine whether the metallic ions of the solution would migrate again to the anode. The solution was not introduced into the middle compartment of the cell until each of the compartments had been partially filled with distilled water and the current turned on. This procedure was adopted in order to avoid any diffusion of the material through the membranes before it was subjected to electrodialysis. The results of the experiment are recorded in table 4. In the case of each of the concentrates many of the ions were found to be transported to the cathode. All of the calcium, practically all of the magnesium, and much of the iron and the aluminum migrated to the cathode compartment during the period of electrodialysis. About equal amounts of silicon were found in the catholyte and the anolyte. Most of the sulfur and practically all of the phosphorus were transported again

TABLE 4

Distribution of the ions of the concentrated anolyte during 144 hours of continuous electrolydialysis

100 gm. of dry soil

PEAT	COMPARTMENT	ORGANIC MATTER*	Si	Fe	Al	Ca	Mg	S	P
		mgm.	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*
A	Cathode	255	0.17	0.72	0.15	0.11	0.11	0.08	0.00
	Middle	528	0.33	0.09	0.00	0.00	0.00	1.70	0.00
	Anode	3742	0.13	0.25	0.16	0.00	0.04	10.38	4.50
		4525	0.63	1.06	0.31	0.11	0.15	12.16	4.50
B	Cathode	47	0.06	0.05	0.11	0.02	0.03	0.03	0.04
	Middle	96	0.02	0.00	0.00	0.00	0.00	0.05	0.02
	Anode	908	0.04	0.00	0.04	0.00	0.00	0.46	3.90
		1051	0.12	0.05	0.15	0.02	0.03	0.54	3.96

* Loss on ignition.

to the anode. Because of the small amounts of sodium and potassium known to be present in the concentrates, no attempt was made to determine the fate of these elements.

In table 4 the sum of the values for the respective ions of the three compartments is shown to agree closely with the value recorded in table 3 for the amount of each ion which was found to be present in a concentrated anode solution similarly prepared. Such an agreement does not hold for the organic matter. The comparison indicates that organic matter was lost from the solutions during electrodialysis.

DISCUSSION

Two explanations might be offered to account for the presence of silicon, sulfur, and phosphorus in the catholyte, and of iron, aluminum, calcium, magnesium, sodium, and potassium in the anolyte, of electrodialyzed peat. The

ions may have migrated to the respective poles as integral parts of organic matter, that is, in chemical combination with it; or they may have been adsorbed by the organic matter and carried mechanically to one or the other of the poles according to the charge of the particles on which the ions were adsorbed.

The metallic ions of the catholyte were found to be independent of the organic matter to the extent that they could be precipitated in the presence of the organic matter. The reverse was true of the metallic ions of the anolyte. These ions appeared to be an integral part of the organic matter. If they were held on the surfaces of the organic matter, it was with such tenacity that they were not released upon digestion with either weak hydrochloric acid or weak ammonium hydroxide. In electrodialyzing the concentrated anode solution, some of the organic matter was destroyed. Presumably, as a result of this action, certain of the metallic ions were released and, acting as free ions, migrated to the cathode. It is probable that the ions were intimately associated with the organic matter.

Sulfur was found to be definitely related to the organic matter and was, no doubt, a part of an organic anion. Conversely, most of the phosphorus was found to be independent of the organic matter, and it is likely that most of the phosphorus was present in the diffusates in the form of phosphate ions.

The presence of organic matter in relatively large amounts in the catholyte is a matter of some conjecture. The diffusion of soluble undissociated organic material through the parchment-paper membrane may have occurred, but an attempt was made to reduce this possibility to a minimum by not turning off the electric current during the period of electrodialysis. If diffusion of this nature did occur it would seem under the influence of the electric current, that the ions would have been redistributed if they were present as free agents or simple ions. Anderson and Byers (1) have stated that the organic matter of certain soils may be dissolved by acids of moderate concentration, and that much of the organic matter thus dissolved is in the form of organic cations. In the present experiment it was observed that much of the organic matter entered the cathode compartment after most of the calcium and the magnesium had been removed from the peat. The acidity of the middle chamber at that time may have been such as to dissolve the organic matter with the formation of organic cations.

Odén (3) and Löddesöl (2) have observed in electrodialyzing soil materials that in certain cases the same kinds of ions migrate to each of the poles. Odén, in reporting the phenomenon with respect to silicon, made no attempt to explain his observations. Finding traces of metallic ions in anolytes, Löddesöl concluded that the hydroxides of the elements had absorbed acid anions. With reference to the present report, the writers are inclined to the view that the metallic ions of the anolyte and the non-metallic ions of the catholyte, with the exception of the phosphate ions, were carried to the cathode and the anode compartment as constitutional parts of organic matter

rather than by the adsorption of the ions on the surfaces of the organic matter. In any event, however, ions of that character constituted only a small proportion of the ions of the diffusates.

If the amounts of the exchangeable ions of the peats are considered in the light of the total amounts of the respective elements of the peats, it is readily discernible that exceedingly large proportions of the elements are in exchangeable form. Only a small percentage of the ions of the diffusates could have been present in the peats as carbonates, sulfates, and phosphates, because of the relatively small amounts of these forms which the peats contained. Thus calcium and magnesium, the predominant exchangeable cations of the peats, are present in the peats largely in exchangeable and in organic form.

SUMMARY

In electrodialyzing peat, ions normally functioning as cations were found in the anolyte, and ions normally functioning as anions were found in the catholyte. Ions of this character were found to be intimately associated with the organic matter of the diffusates. The results of the investigation suggest that these ions were transported to the respective poles as integral parts of organic matter rather than as adsorbed particles on the surfaces of organic matter.

Most of the exchangeable cations of the peats were found to have been present in the peats as ions of organic salts. Practically all of the sulfur was found to be a component of the organic matter, whereas most of the phosphorus appeared to be in the form of phosphate ions.

REFERENCES

(1) Anderson, M. S., and Byers, Horace G. 1933 Character and behavior of organic soil colloids. U. S. Dept. Agr. Tech. Bul. 377.

(2) Löddesöl, Aasulv 1932 Investigations concerning separation of similarly charged ions from soils by electrodialysis. *Soil Sci.* 33: 375–395.

(3) Odén, Sven 1927 Om jordens surhetsgrad, buffertverkan. och kalkbehov. *Meddel.* 318: 1–88. *Centralanst. Försöksv. Jordbruksområdet* [Sweden].

(4) Wilson, B. D., and Staker, E. V. 1935 Ionic exchange in peat soils. N. Y. (Cornell) Agr. Exp. Sta. Mem. 172.

(5) Wilson, B. D., and Staker, E. V. 1935 Complex ions in relation to the electrodialysis of peat. *Trans. Third Internatl. Cong. Soil Sci.* 1: 426–428.

THE "CHEMICAL ANALYSIS" OF THE SOIL[1]

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The greater the crop yield of the soil in any country, the more attention must be paid to returning to the soil the plant materials removed, if these are no longer present in sufficient quantities and high yields are still expected. Since, however, it is not known what the soil contains in the way of plant nutrients, nor what has been removed during the past, it is necessary to investigate the soils for their content of plant nutrients.

For the nitrogen content, especially the nitrogen requirements, field experiments offer the best and most reliable information. For the lime requirements of the soil, a simple reaction determination is sufficient. The P and K requirements of the soil are difficult to determine for the following reasons: Field experiments are not sufficient because of the high activity factor of these nutrients, and the so-called chemical methods are not as yet efficient. In field experiments it often happens that during the season of fertilizer additions no increase in yield takes place; but if no additions of nutrients were made, the yield would drop the following year. It often happens that the quantity of nutrients in the soil is sufficient to produce a maximum crop the year of the experiment. The nutrients may, however, be exhausted the year following. In laboratory experiments we fail to bring into solution those elements which might be utilized by the next year's crop. If we were able to bring these nutrients into solution such analyses would present no difficulties.

Field experiments are the standard. Soil analyses are important for the evaluation of cultivated land, and they are important for the farmer who is looking for advice about fertilizers. The field experiment, however, as pointed out, fails under certain conditions. To obtain reliable results, it is necessary to decrease the nutrient content of the soil to a very low level. This may be accomplished either by using a shallow layer of soil, thus decreasing the quantity of soil which actually supplies the nutrients to the plants, or by "diluting" the soil with sand, free of nutrients.

Both of these methods are applicable to the soil removed from its natural position. Perhaps the top soil only should be removed, and investigated in the laboratory as any other soil. Top soil in containers 80 cm. deep supplies to the plants, under conditions in Prussia, only half the amount of nutrients,

[1]Translated from the German by Mordecai Hoseh and J. S. Joffe, New Jersey Agricultural Experiment Station.

because this depth equals only half of the soil depth under normal field conditions. If one third of this soil (by volume) is mixed with two-thirds of sand free of nutrients, the pot cultures will have at their disposal a layer of only about 6 cm. of soil, and only one-sixth of the nutrients found under field conditions. If under these conditions there is no response to fertilizers, say to phosphoric acid, it would indicate that since we have at the disposal of the plant just one-sixth of the soil, the latter under field conditions contains six times the amount of nutrients required to produce a maximum yield. Hence, from plant physiological considerations after subtracting the amount of nutrients used up during the year of the experiment, the conclusion is that the soil contains enough nutrients to produce a maximum crop for five years more.

If, on the other hand, the addition of phosphoric acid in the pot experiments results in an increase of yield, then it is possible to compute the phosphoric acid content of the soil from the yield data of the unfertilized crop, taking in consideration the activity laws of the growth factors. If the amount thus obtained be multiplied by 6, we have the field content of the respective nutrient. The value so derived is based on purely plant physiological methods.

We thus see that it is only the plant which could indicate whether or not a given soil requires fertilization. Results obtained by any of the laboratory methods should, therefore, be compared with those derived from crop yields. It is a source of satisfaction to feel that it is possible to investigate soil samples by plant physiological, as well as by laboratory method. Thus the criteria of the validity of any laboratory method, be it chemical or microbiological, are the results obtained from fertilizer experiments in pot cultures, which results are interpreted by the activity law of the growth factors.

On the basis of the discussion presented, the joint meeting of the Second, Third, and Fourth Commissions of the International Society of Soil Science, held in Copenhagen in 1933, unanimously resolved to investigate the reliability of various laboratory methods for potassium and phosphorus requirements of soils. The first results of these investigations were discussed at the meeting in Königsberg in July, 1936.

It is very significant that any of the methods may be applied to both poor and rich soils. It is self-evident that no phosphoric acid can be found in a soil which contains none; on the other hand, if there is much of it, each method should reveal its abundance. Most soils, however, are types between these two extremes, and it is with these that some of the methods will prove better than others. It is in this connection that we should enrich our knowledge for the farmer's sake. From the aforesaid, it becomes apparent that to accomplish this a great number of different soils should be investigated, and the results compared with the ones obtained in pot experiments.

The question may be asked, Why do we need chemical or laboratory methods and why should we not limit ourselves to pot experiments? The answer is that in the case of pot experiments the time element is a factor which causes excessive expense. Also, it is necessary to test countless numbers of soils,

which necessitates a cheaper and more rapid method. At any rate the method should be *absolutely reliable*, or else no testing should be undertaken.

It is hoped that the International researches will furnish reliable results in perhaps 80 per cent of all cases. If such results are achieved, there would remain only 20 per cent of soils to be tested by the pot culture method. Applying laboratory methods it would be possible to investigate in Eastern Prussia 10,000 soils annually, instead of the 2,000 which now are examined, involving the use of 20,000 culture vessels. Thereby the cost of the investigation would be considerably lowered, to the ultimate benefit of agriculture.

HEAT OF WETTING OF SOME SOIL COLLOIDS AT DIFFERENT MOISTURE CONTENTS

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The phenomenon of liberation of heat on wetting of dry powders was observed as early as 1802 by Leslie. It is often referred to as the "Pouillet's Effect" after Pouillet (5), who confirmed Leslie's observations. Since then considerable work has been done in this field, and several theories advanced.

This investigation deals with the heat of wetting of several soil colloids containing different amounts of water.

METHOD AND PROCEDURE

The materials investigated were four colloids separated from Californian soils. They were Altamont–605, Yolo–612, Vina–618, and Aiken–630. These colloids were separated by sedimentation following vigorous stirring in water, without the addition of any dispersing agent. The partial analyses of the colloids used are given in tables 1 and 2. These colloids vary in their silica-sesquioxides ratio, exchangeable bases, and organic matter content, all of which influence the heat of wetting. It seemed necessary for this experiment to have the exchangeable bases uniform, and to remove as much of the organic matter as was possible without seriously affecting the colloid. The latter was accomplished by using 6 per cent H_2O_2, and by heating the colloid on a steam bath for about 24 hours. The exchangeable bases were replaced by H. The colloids removed from the steam bath were treated with 0.049 *N* HCl using 1.6 l. of the acid for each 10 gm. of colloids (80 m.e. of H per 10 gm. of colloid). The filtrate was removed by a Pasteur-Chamberland filter battery. After the HCl was run through, the filtrate was tested for Ca with oxalate, and if none was found the washing with distilled water was begun. This last operation was continued until no more Cl was found. The sample then was dried for 24 hours at 110°C., and the loss by solution was determined. The filtrate from the acid treatment was collected, and the total sesquioxides removed from the colloid were determined. The "solution loss" and "R_2O_3 loss" columns of

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The writer takes this opportunity to thank Dr. G. B. Bodman for his helpful suggestions in planning and carrying on the experimental work.

[2] Thesis submitted to the faculty of the University of California in partial fulfillment of the requirements for the degree of Master of Science.

table 1 give the values thus found. The method described in Washington's *The Chemical Analysis of Rocks* (7) was employed in the determination of the sesquioxides. The figures in the "solution loss" column of table 1 include organic matter and sesquioxides removed in solution, and the difference in weight between the exchangeable bases originally present and the substituted hydrogen. The colloids thus prepared were oven-dried and ground up in an agate mortar to pass a 0.1 mm. mesh. A uniform starting point with regard to water content was effected by exposing the samples in desiccators to water

TABLE 1

Partial composition of colloids as determined by fusion analysis

COLLOID	LAB. NO.	FORMATION	DEPTH	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	IGNITION LOSS	MOLAR $\frac{SiO_2}{R_2O_3}$	MOIST. CONT. DRIED AT 110°	SOLUTION LOSS	R_2O_3 LOSS
			cm.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*		*per cent*	*per cent*	*per cent*
Altamont..	605	Primary	20–45	50.5	0.53	22.6	9.49	3.96	2.70	.....	3.67	8.31	16.2	1.56
Yolo.....	612	Secondary	18–42	49.4	0.48	20.6	10.4	1.29	5.68	9.38	3.08	7.37	16.3	....
Vina.....	618	Secondary	46–60	43.4	0.50	26.0	13.7	1.28	2.55	10.8	2.11	8.36	13.6	1.73
Aiken.....	630	Primary	15–42	39.5	0.10	35.1	10.7	0.63	0.32	13.9	1.60	4.65	7.3	0.83

TABLE 2

Partial composition of soils from which colloids were extracted, their total NH_4 absorbing capacity, and the bases displaced by 1 N $NH_4C_2H_3O_2$ expressed in milliequivalents per 100 gm. of soil

SOIL	CLAY CONTENT	MOISTURE OVEN DRY BASIS*	TEST FOR CO_3†	NH_4 ABSORBING CAPACITY	BASES DISPLACED				
					Ca	Mg	K	Na	Total
	per cent	*per cent*		*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*
605	50.3	5.28	High	32.94	64.54	6.71	2.77	0.93	74.95
612	31.6	2.16	Present	27.20	30.77	24.24	1.28	2.15	58.44
618	25.9	4.88	None	25.64	17.81	11.80	0.84	0.59	31.04
630	38.2	3.68	Trace	12.11	3.31	2.05	1.61	Trace	6.97

* Below 110°C.

† Carbonate content by dilute HCl.

vapor over 3.3 per cent H_2SO_4 for 5 to 7 days at 30°C. The desiccators in which the colloids were kept were previously evacuated to give a total pressure of 0.5–0.7 cm. of mercury. After this time had elapsed the samples were removed from the desiccators and submitted to the desired temperatures. The heat of wetting was investigated over a range of moisture contents obtained by heating the colloids at various temperatures between the room temperature and 500°C. An electric oven was used for the temperatures up to 200°C., and a muffle for the range above 200°C. The samples were exposed to any given

temperature for 24 hours. Pyrex glass bottles were used in heating the samples up to 500°C., and for higher temperatures quartz bottles were used. Two sets of samples were heated simultaneously at each particular temperature. Of these one set was used for heat of wetting determination, and the other for moisture content determination. A single set of samples was used throughout the experiment for determination of water content. The bottle holding the sample was weighed after each heating, and the loss in weight was taken as moisture loss at this particular temperature. It should be said here that the previous heating at lower temperatures has no significant influence upon that which follows, for a certain amount of water is removed at each particular temperature regardless of the history of drying. For example, if a sample were dried at 50°C., then at 60°C., then at 110°C., for 24 hours at each temperature, and a similar sample were dried for 24 hours at 110° only, then the sum of the amounts of moisture removed at each temperature in the former case is equal to the amount removed at 110° in the latter case. This has been proved in a preliminary experiment over a rather wide range of temperatures. Use will be made of this elsewhere.

The sample to be used for heat of wetting determination, after removal from the oven, was tightly stoppered and cooled over $CaCl_2$, and then weighed. The empty bottle was weighed again after the sample was transferred to the calorimeter, and thus the weight in grams of the materials used in the calorimeter was determined.

The heat of wetting was measured in a special calorimeter. This consisted essentially of a Dewar flask comprising the wetting chamber (A), to which was connected by a ground glass joint (B) a reservoir (C), and an airline (D). A three-way stopcock (E) permitted connection to either the water reservoir or to a Cenco Hyvac pump, or complete sealing of the calorimeter chamber. A thin-walled glass tube (F) was sealed into the neck of the vessel and extended down to the bottom of the chamber for the purpose of admitting a thermoelement (G). Plate I and figure 1 represent the calorimeter and the set-up.

To expedite the work two such calorimeters were used. The temperature changes taking place on wetting, as well as the initial temperature of the colloid and the water, were measured by means of two thermoelements of six couples each, and a White Double Potentiometer. The thermoelements were especially prepared for this purpose and were made from copper and constantan no. 36 and 30 gauge wire, respectively. In order to obviate the determination of the water equivalent of the two calorimeters, and to eliminate the value of the specific heat for the colloid, which at the best is only an average, an electric heater was used (plate 1, H).

The following procedure was used: The calorimeter was thoroughly washed and rinsed with distilled water. Next it was rinsed with absolute alcohol to remove the water, and finally it was rinsed with ether, which rendered the calorimeter dry. The sample was then transferred to the calorimeter chamber, and the upper part was quickly put on. By using the 3-way stopcock the

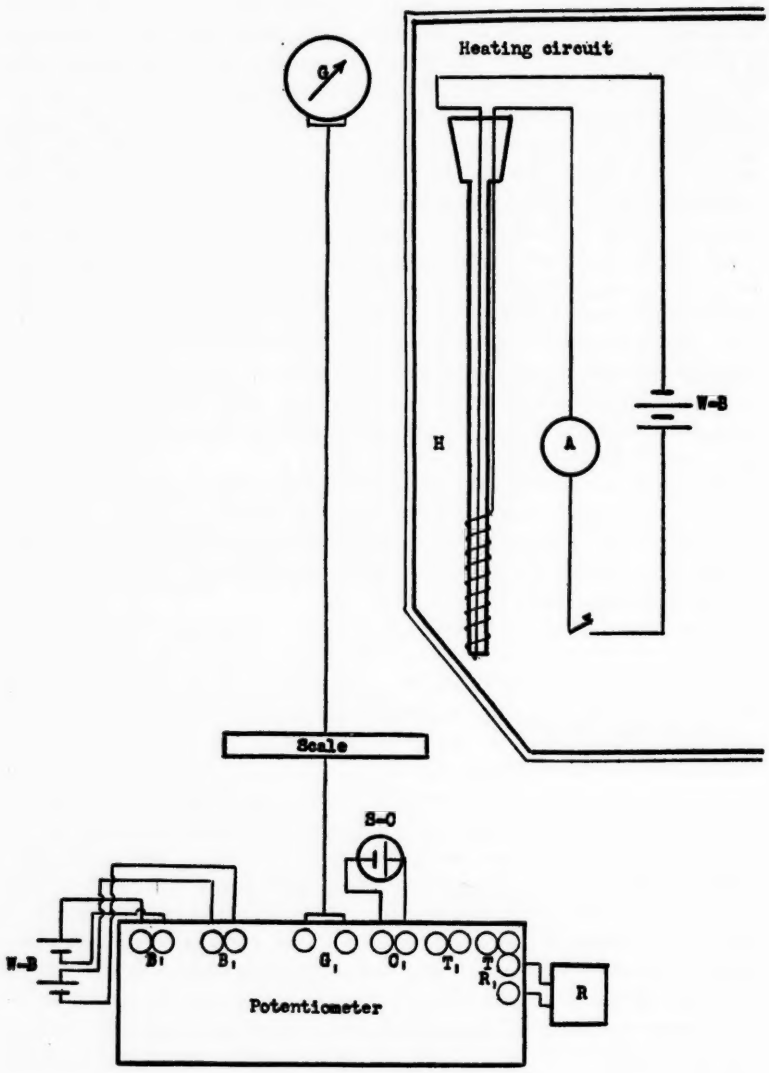


FIG. 1. SET-UP AND WIRING

A, Milliammeter; *G*, Galvanometer; *H*, Heater; *R*, Resistance box; *S-C*, Standard cell; *W-B*, Working battery.

Binding posts: *G*, Galvanometer; *C*, Standard cell; B_1, Working batteries; R_1, Resistance box; T_1, Thermoelements.

calorimeter was evacuated for 10 to 15 seconds. This was done to facilitate the admission of water and a rapid, thorough wetting of the colloid, thereby hastening the reaction. The water was next poured into the water reservoir, the thermoelements inserted in their proper places, and enough time allowed for the system to come to a constant temperature. In each case 25 cc. of water, measured out of a burette, were used. A mixture of ice and water was used as reference point for the thermoelements. The E.M.F. due to differences in temperature between the "business ends" immersed in the water and sample, respectively, and the reference point, were recorded, in each case after the E.M.F. became constant. The water was admitted, and again when the E.M.F. became constant, recorded as the reaction E.M.F. The change due to the reaction is given by

$$\Delta E = E - E^{\circ} \qquad (A)$$

where ΔE is the change in microvolts, E is the final E.M.F. and E° the initial E.M.F. due to the difference in temperature between the sample and the ice water. After E was recorded the upper portion of the calorimeter was removed, and the heater inserted. Again the initial E.M.F., E°_1, was read; the heating circuit was closed, and a stopwatch started simultaneously. The current was measured by using a milliammeter, and after 2 to 3 minutes the circuit was opened and the watch simultaneously stopped. The calculations were made from the following relationships

$$1 \text{ calorie} = 4.186 \text{ watt-sec.} \qquad (B)$$

$$1 \text{ watt} = 1 \text{ volt-ampere} \qquad (C)$$

$$\text{total energy input} = I^2 \times R \qquad (D)$$

Hence the total input of energy in calories is given by

$$\text{calories} = 4.186 \times I^2 \times R \times t \qquad (E)$$

R was carefully determined, I was read on the milliammeter in the heating circuit, and the time t was obtained by means of a stopwatch.
For the heating circuit we can write, as in equation (A)

$$\Delta E_1 = E_1 - E^{\circ}_1 \qquad (F)$$

where E°_1 and E_1 are the initial and final E.M.F., respectively. The former is used after equilibrium is established with the heater inserted and the circuit open. The latter (E_1) is used after closing the circuit and letting the current I pass for t seconds.

The relationship between the microvoltage produced and the corresponding heat energy in calories can thus be established, and the measured microvoltage may be interpreted in calories liberated during the wetting reaction. Since the E.M.F.-temperature relationship is linear over the range of temperature during the experiment, we may put

$$r = \frac{\text{cal}}{\Delta E_1} \text{ calories per microvolt} \qquad (G)$$

The calories evolved on wetting equal

$$r \Delta E \qquad (H)$$

If M is the mass in grams of the sample wetted then

$$H = \frac{(r\Delta E + a)}{M} \text{ cal/gm.} \qquad (I)$$

where a is a correction to be made for the difference in temperature of the sample and the water. The value of a is obtained in the following way: the initial E.M.F. due to the temperature of the water and of the sample, respectively, as compared to the ice water, were converted by means of a deviation curve and standard tables to degrees Centigrade (6).[3] The difference in degrees Centigrade multiplied by the mass of water used gives the amount of calories $= a$ to be added or subtracted.

The total moisture loss was computed by adding up all the losses in weight between room temperature and 500°C. The weight of the sample at 500°C. is taken as dry weight. From these two values (total moisture loss and dry weight) and the loss in weight for each particular temperature of heating, the moisture content associated with each particular temperature of heating was computed.

Before starting the heat of wetting determinations on the four samples of colloid, the reproducibility of results was ascertained for measurements made exactly as described above. The heats of wetting of 11 samples of a Stockton colloidal clay, previously heated for 24 hours at 110° C., were determined for this purpose. The results follow:

Sample	*Cal./gm.*
1	11.42
2	11.63
3	11.47
4	11.58
5	11.39
6	11.50
7	12.01
8	11.47
9	11.45
10	11.38
11	11.41
Mean.....	11.52

By taking the sum of the deviations from the mean of each determination and dividing by the number of determinations, we obtained a mean deviation of 0.12, or a mean relative deviation of 1.04 per cent.

[3] The deviation curve is obtained by plotting the E.M.F. observed as abscissa vs. ΔE as ordinate, in calibrating a thermoelement. ΔE is obtained by subtracting the standard E.M.F. from the observed E.M.F. $\Delta E = E_{obs} - E_{stand.}$ where $E_{stand.}$ for a given temperature is taken from the tables. The actual E.M.F. is then obtained by subtracting ΔE from $E_{obs.}$ when it is converted into degrees Centigrade by means of the standard tables.

The determinations of heats of wetting of samples dried up to 110°C. are averages of closely agreeing duplicates. The others are all single determinations, except for the values of maximum heats of wetting for each sample.

RESULTS

In this investigation the purpose was to correlate the heat of wetting with the amount of water present on the surface of the material. In speaking of the surface of a soil colloidal particle it is desirable to explain what is meant by it. We do not think of such a surface as being continuous as, for instance, is that of a rigid sphere. Indeed, the surface of a soil colloidal particle may be conceived as having many openings, or micropores. It is thus obvious that the energy required to remove a given amount of water from the surface may be different for different parts of it. It will be necessary to spend more energy to drive off a molecule of water from a micropore than from the "outer surface," other conditions being equal.

Since the samples used for moisture determination were to be submitted to a series of temperatures consecutively higher, it became necessary to ascertain whether the history of drying has any influence on the amount of water removed. For this purpose duplicate samples of Stockton colloidal clay were submitted to temperatures between 40°C. and 500°C. and kept at each temperature for 24 hours before changing to a higher one. The method was as follows: two samples, (*a*) and (*b*), were placed in the oven at 40°C. After 24 hours the samples were weighed and the temperature raised to 50°C. These samples were returned to the oven, and two new ones added. This was done at all the other temperatures. The same member of each pair of samples was always weighed, once after 12 hours and the second time after 24 hours, before the temperature was changed.[4] Tables 3 and 4 give the results obtained. The former presents the values for each pair at each particular temperature; the second, the averages of all samples for the same temperature, and the extreme deviations from the mean. The amount of loss at 110°C. was taken as 100 per cent, and from this all the other values were computed. Although similar results were obtained for temperatures above 110°C., they are not included here for the reason that neither the organic matter nor the carbonates of this colloid were removed, and oxidation of the former and decomposition of the latter could set in at higher temperatures, and the values would be reliable no longer.

From the results stated in tables 3 and 4 we may safely conclude that the dominant factor in removal of water from soil colloids is the temperature, and not the time. The latter enters only in the consideration of equilibrium conditions for each particular temperature.

Table 5 gives the percentages of water removed from, and remaining associated with, the soil sample by heating at different temperatures. Columns

[4] The second member was weighed only after 24 hours.

TABLE 3

Percentage of moisture removed from the colloid at each temperature

Amount removed at 110°C. taken as 100 per cent

TEMPERATURE	A	B	A	B	A	B	A	B	A	B	A	B	A	B
°C.	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
40	34.82	34.48												
50	18.46	18.87	52.47	51.02										
Total	53.28	53.35	52.47	51.02										
60	11.34	10.88	12.23	13.80	65.48	64.86								
Total	64.62	64.23	64.70	64.82	65.48	64.86								
70	13.10	12.87	12.48	11.99	11.63	11.79	78.65	77.21						
Total	77.72	77.10	77.18	76.81	77.11	76.65	78.65	77.21						
80	6.72	6.76	7.21	8.03	7.85	7.98	6.47	7.39	85.70	84.72				
Total	84.44	83.86	84.39	84.84	84.96	84.63	85.12	84.60	85.70	84.72				
90	6.48	6.01	6.34	6.02	6.22	6.33	6.29	6.57	5.68	6.75	92.31	91.87		
Total	90.92	89.87	90.73	90.86	91.18	90.96	91.41	91.17	91.38	91.47	92.31	91.87		
110	9.03	9.13	9.22	9.14	8.79	9.04	8.58	8.83	8.62	8.53	7.69	8.13	100.0	100.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100 0	100.0

2, 5, 8, and 11 give the per cent of dry weight of the sample. It will be recalled that by dry weight here is meant the weight of the sample heated at 500°C. The reason for selecting this temperature is that no significant heat of wetting was obtained with samples previously heated at this temperature. Strictly

TABLE 4

Percentage of moisture removed at different temperatures

Means and deviations

TEMPERATURE	NUMBER OF SAMPLES	MOISTURE REMOVED		
		Mean	Maximum value	Minimum value
degrees		*per cent*	*per cent*	*per cent*
40	2	34.65	34.82	34.48
50	4	52.53	53.35	51.02
60	6	64.95	65.48	64.62
70	8	77.43	78.65	76.65
80	10	84.83	85.70	84.39
90	12	91.26	92.31	90.73
110	14	100.0	100.0	99.95

TABLE 5

Percentage of moisture removed and remaining on the soil colloids after drying at different temperatures

TEMPERATURE	ALTAMONT			YOLO			VINA			AIKEN		
	Removed			Removed			Removed			Removed		
	Dry weight	Total moisture	Residual	Dry weight	Total moisture	Residual	Dry weight	Total moisture	Residual	Dry weight	Total moisture	Residual
degrees	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Room	0.0	0.0	100.0	0.0	0.0	100.0	0.0	0.0	100.0	0.0	0.0	100.0
47	16.73	42.07	57.93	14.52	43.57	56.43	13.16	33.00	67.00	21.02	45.85	54.15
70	28.22	70.97	29.03	24.26	72.93	27.07	26.57	66.51	33.49	29.44	64.23	35.77
110	30.32	76.25	23.75	26.03	78.12	21.88	28.49	71.41	28.59	30.20	66.06	33.94
200	32.31	81.58	18.42	27.21	81.65	18.35	30.63	76.76	23.24	31.89	69.57	30.43
340	35.85	90.17	9.83	29.70	89.14	10.86	33.24	83.30	16.70	37.20	81.16	8.84
400	37.82	95.11	4.89	32.55	97.67	2.33	36.53	91.43	8.57	44.19	96.40	3.60
500	39.76	100.0	0.0	33.32	100.0	0.0	39.90	100.0	0.0	45.83	100.0	0.0

speaking this point is not at 500°C. but lies somewhere between 400°C. and 500°C. In order to find the exact temperature corresponding to the point of complete dehydration, the region between 400°C. and 500°C. would have to be thoroughly explored. Figure 2 presents the above facts graphically. On this diagram the water loss (Δw) in per cent between any two temperatures, divided by the increase (Δt) in degrees Centigrade between these two tempera-

tures, was plotted against the mean (t_m) of the two temperatures measured. By inspecting these curves we see that the amount of moisture removed per degree Centigrade decreases as the temperature increases until it reaches a minimum at about 160°C. Then it begins to rise, reaching a second maximum at about 370°C., after which it falls off. It may be recalled here that similar results were obtained by Baver and Horner (1).

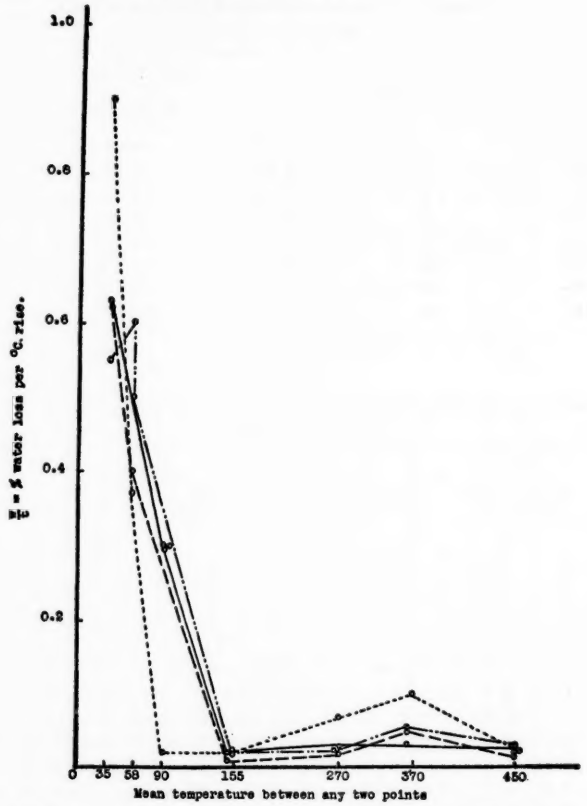


FIG. 2. LOSS OF WATER IN PER CENT PER DEGREE CENTIGRADE RISE

O————O, Altamont; O- - - -O, Yolo; O—·—··O, Vina; O----------O, Aiken.

Table 6 presents the heats of wetting of the soil colloids concerned at different moisture contents. The maxima found by heating at 340°C. to 400°C. which corresponds to moisture contents as per cent of total removed at 500°C. are:

Altamont	66.93 cal/gm.	9.83 per cent
Yolo	65.13 cal/gm.	10.86 per cent
Vina	45.49 cal/gm.	8.57 per cent
Aiken	55.60 cal/gm.	3.60 per cent

TABLE 6

Heat of wetting of soil colloids at different moisture contents

TEMPERATURE	ALTAMONT		YOLO		VINA		AIKEN	
	Moisture left	Heat of wetting	Moisture left	Heat of wetting	Moisture left	Heat of wetting	Moisture left	Heat of wetting
degrees	*per cent*	*cal./gm.*	*per cent*	*cal./gm.*	*per cent*	*cal./gm.*	*per cent*	*cal./gm.*
Room	100.0	2.45	100.0	1.45	100.0	.....	100.0	0.99
47	57.93	3.88	56.43	1.94	67.00	2.81	54.15	1.09
70	29.03	5.53	27.07	4.39	33.49	6.33	35.77	6.36
110	23.75	10.59	21.88	9.10	28.59	15.45	33.94	10.96
200	18.42	11.01	18.35	18.03	25.24	15.19	30.43	8.32
340	9.83	.....	10.86	65.13	16.70	41.00	8.84	43.89
400	4.89	34.23	2.33	61.13	8.57	45.49	3.60	55.60
500	None	7.34	None	None	None	3.50	None	None

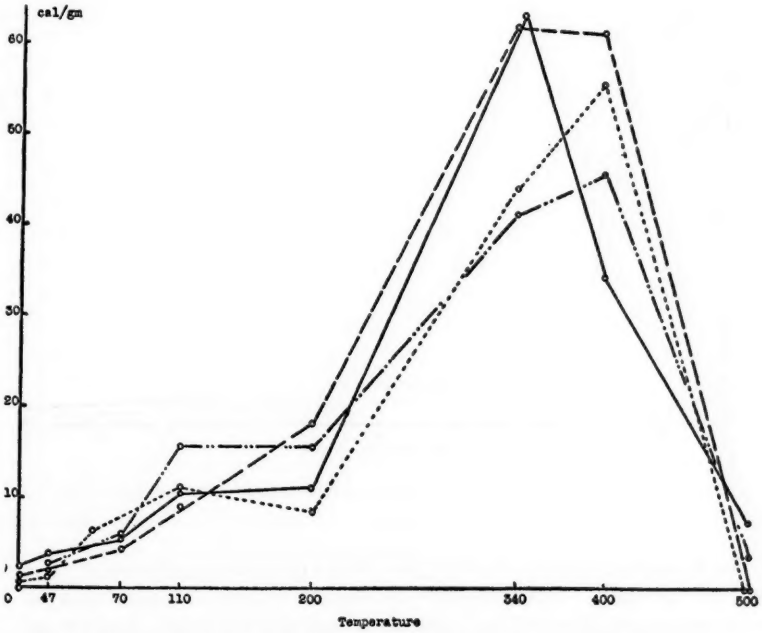


FIG. 3. HEAT OF WETTING OF SOIL COLLOIDS HEATED AT DIFFERENT TEMPERATURES
O———O, Altamont; O- - - -O, Yolo; O—·—·—·O, Vina; O----------O, Aiken.

It can be seen that when the moisture content is reduced beyond a certain value, the heat of wetting decreases rapidly and becomes zero, or thereabout. It is probable, however, that by heating the soil colloid at a temperature at which it would give maximum heat of wetting, or even at a temperature at

which it would give no heat of wetting, not all of the water of the soil colloid is driven off. This point will be discussed in more detail later.

Figure 3 presents the heat of wetting in calories per gram obtained by heating the samples at different temperatures. We see that at first there is an almost linear increase, then there is a range of temperatures between 110° and 200°C. where very little variation is observed in the evolution of heat with the increase of temperature, except with Yolo. Then follows a rapid increase to a maximum, and the heat of wetting drops off suddenly at 340° to 400°C.

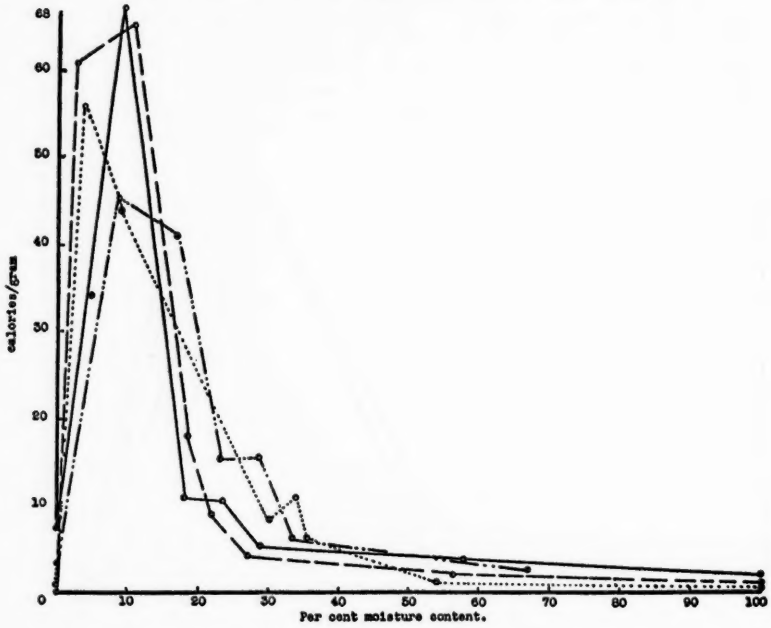


FIG. 4. HEAT OF WETTING OF SOIL COLLOIDS AT DIFFERENT MOISTURE CONTENTS
O————O, Altamont; O- - - -O, Yolo; O—·—·—·O, Vina; O----------O, Aiken.

Figure 4 gives the heat of wetting in calories per gram at different relative moisture contents. Transformation to absolute amounts of water may be made from figure 4 by reference to table 5, from which it is seen that 100 per cent moisture corresponds to 39.76, 33.32, 39.90, and 45.83 grams of water per 100 grams of the Altamont, Yolo, Vina, and Aiken, respectively, at 500°C. From this diagram it can be seen that the rate of increase of the heat of wetting is very slow until 60 to 70 per cent of the water is removed. Then there is a rapid increase to a maximum coinciding with the moisture content of 4 to 10 per cent, after which it falls rapidly off.

DISCUSSION

The evolution of heat on wetting certain powders is a display of energy inherent in their surface properties. It is immaterial whether one accepts the theory of physical adsorption, or polar adsorption, or changes in surface free energy (4); surface relationships are concerned although different investigators view the character and nature of the surface differently. All of those who worked with water and other liquids as wetting agents arrived at the conclusion that in the case of the former the heat of wetting is most strongly pronounced. The affinity of the soil colloids for water is indeed great. If a dry sample of a soil colloid be exposed to air which is at a higher humidity than the soil colloid, the colloid will take up moisture from the air. Muntz and Gaudechon (3) have shown that a clay sample competed successfully with alcohol for water. In these experiments heat was evolved when samples exposed for 5 days to vapor tension over 3.3 per cent H_2SO_4 were wetted. This is not in accord with Mitscherlich's (2) definition, for according to him no heat of wetting should be observed at that degree of moisture. It seems, however, that at least theoretically, heat should be evolved, because it is known that soil colloids will absorb water if exposed to a vapor tension over 3.3 per cent H_2SO_4 far beyond 5 days.

Theoretically we can imagine a condition at which the attractional forces of the colloid for water will be satisfied, and then no more water will be absorbed. Obviously at this point there would be no heat of wetting. The cations most commonly found associated with the soil colloid particle, forming the so-called diffused outer layer, are: Ca, Mg, Na, K, and H. These cations will attract water differently, depending on their size, hydration, etc. If, however, H is substituted for all the cations found on the surface, then the attraction over the surface due to the character of the cation will be uniform. We may safely assume that the water on the surface is arranged in molecular layers. Obviously different layers will be held to the surface with varying degrees of intensity decreasing from the solid-water interface outwards. By applying energy, e.g., heat, we shall "strip off" one or more such layers. The amount removed, other conditions being equal, depends entirely upon the amount of energy supplied. By doing so we have increased the attractional forces of the particle. The intensity with which it will attract water now depends on the amount remaining on the surface. We see thus that these two forces, namely, the one required to move a certain amount of water from the colloidal particle, and the one displayed when this amount of water is again being taken on, are proportional to each other and probably equal but opposite in direction.

The experimental results are in accord with the well known facts that: (*a*) The higher the temperature at which the sample is heated, i.e., the greater the energy applied, the greater is the amount of water removed from the colloid. (*b*) The greater is the quantity of removed water, the greater the heat liberated on wetting, i.e., the greater the energy of attraction.

Unfortunately, in the present investigation there was no means of establishing the exact relationship between these two forms of energy. By further examining the results it is seen that although at first increases in temperature of heating cause increases in the heat of wetting, yet a temperature is finally attained corresponding to the liberation of the maximum energy on wetting. Further heating is followed by a decline in liberated energy on wetting, which soon falls off to zero or thereabout.

The surface of the soil colloidal particle remains active as long as it remains unaltered. Replacing reactions may affect the intensity of the surface activity, yet they will not destroy it. The surface can be rendered inactive, for example, by excessive heating. Here the sintering turns the surface entirely inactive, as is seen by the fact that there is no heat of wetting evolved.

Two of the samples, Yolo and Aiken, were heated to 1000°C. No evolution of heat on wetting appeared, but at successive stages there was a loss in weight. The other two samples were also heated to this temperature, without determining the heat of wetting, and they likewise showed consecutive loss in weight. In this experiment there was no means for establishing the nature of this loss. It could not be attributed to a loss of chemical components, for the temperatures of sublimation of the elements making up the micelle are above 1000°C. This loss in weight, however, could possibly be attributed to water.

We may conceive of three kinds of water being associated with the soil colloidal particles:

1. The water of adsorption, including the water of hydration of the exchangeable ions. This water is the most active as far as heat of wetting is concerned, and its removal will result in evolution of heat upon wetting.

2. Water of crystallization, associated with the compounds making up the micellar core. Its removal would result in disrupting the core. It is uncertain at present whether it plays any rôle in heat of wetting although evidence is lacking.

3. Potential water, which can possibly be formed from the hydrogen and oxygen present in the compounds of the micellar core as such, and not ordinarily combined as water. At the more elevated temperatures when enough energy is supplied they may, however, combine and be driven off. Potential water probably plays no rôle in the heat of wetting effect. For conceivably when this water begins to come off, the particle is altered to such an extent that it is no longer able to give heat on wetting, i.e., the affinity of the particle for water has been destroyed. The loss in weight with increased temperatures after no heat of wetting appeared could possibly be explained by the loss of potential water, and perhaps all or some of the water of crystallization. This would be in accord with the findings of Baver and Horner.

By inspecting the curves, figures 3 and 4, certain inferences can be drawn. The first thing one can notice is that generally speaking the four colloids can be divided into two groups. In one we have Altamont and Yolo, in the other, Vina and Aiken. The apparent differences between them are:

(*a*) The maximum values for the heat of wetting are greater for the Altamont and Yolo than for Vina and Aiken, viz., 66.93 and 65.13 cal/gm. as compared with 45.99 and 55.60 cal/gm.

(*b*) These maximum values appear at different temperatures for the two groups; for Altamont and Yolo they coincide with 340°C., and for Vina and Aiken, with 400°C. of heating.

(*c*) Altamont and Yolo exhibit a maximum heat of wetting at a higher moisture content than the other two, namely, 9.83 and 10.86 per cent, as compared to 8.57 and 3.60 per cent.

These differences in behavior can be attributed to the differences in the chemical composition of the four colloids.

It is customary in soil investigations to use the silica-sesquioxide ratio in explaining differences in chemical behavior. The question is raised whether the composition as expressed by this ratio is, per se, responsible, or whether it is not rather the result of the greater abundance of the replaceable cations which produce such effects and which in turn are governed by this ratio.

For the purpose of this experiment it seems logical to differentiate, although fully aware of the interrelation, between the silica-sesquioxide ratio and the amount of exchangeable bases. The reason for this differentiation is that while the exchangeable bases will determine the amount of water held at the outside of the soil colloidal particle, the silica-sesquioxide ratio will determine the amount of water (chiefly water of crystallization and potential) present in the inside of the particle.

Although the water held by the exchangeable cations plays a rôle in the magnitude of heat of wetting, as mentioned under 1, the "inner" water of both crystallization and potential may not influence the heat of wetting, or rather, when they begin to come off, the ability of the particle to give heat of wetting may be destroyed. Thus, although a higher base content will have higher values for maximum heat of wetting, when heated at temperatures beyond the one at which the maximum heat of wetting is obtained, soil colloids with higher silica-sesquioxide ratios are apt to lose more water. This is the same as saying that at the maximum heat of wetting the soil colloids having a higher silica-sesquioxide ratio have a higher (total) water content.

The curves obtained in this experiment, figures 3 and 4, show three definite regions: one extending up to about 110°C. and coinciding with a moisture content of about between 35 and 100 per cent (in the sense used in this experiment); the second found when heated at temperatures between 110 and 200°C. and corresponding to moisture content between about 25 and 35 per cent; the third lying between the temperatures 200°C. and 400°C. and moisture contents of about 13 to 25 per cent. This last region is less precise than the other two.

The first region is characterized by an almost linear relationship between the heat of wetting and the temperature of heating or moisture content, respectively. The second shows no marked increases in the heats of wetting

with the rise in temperature (fig. 3) except for the Yolo, which behaves differently from the other three colloids and, as seen from figure 2, the ratio of removal of water in this region is the smallest. Then follows a region of rapid increase of the heats of wetting with the rise in temperature of heating, and finally a rapid fall of the heat of wetting values.

The region of the rapid decline of the heat of wetting values is doubtless connected with the disrupture of the crystal lattice of the soil colloidal particle.

The exact nature of the other regions is harder to explain without further investigation. At the present it can only be said that the shape of the curves in this region is determined by the nature of the water left associated with the particle, and by the nature of the surfaces of the colloidal particle (micropores and crevices) which determines the magnitude of the forces by which the water is held.

CONCLUSIONS

From the preceding experimental data the following conclusions may be reached:

1. In heating the soil colloid the amount of water removed depends, other conditions being equal, on the temperature of heating; the history of drying is unimportant.

2. Drying at 110°C. does not remove all of the water found on the surface of the soil colloidal particle.

3. The higher the temperature of heating over the range investigated, i.e., the more energy that is applied, the more water there is removed.

4. The more water that is removed from the soil colloidal particle, the greater is the force with which the particle will attract water, provided it is not rendered inactive.

5. These two forces are proportional, and there is reason to believe that they are equal and opposite.

6. Heat of wetting will be evolved as long as the internal structure of the soil colloidal particle remains unaltered; in this experiment this alteration set in when the colloids were heated above 400°C.

7. When the nature of the colloidal particle becomes destroyed, as by sintering, there will be no heat evolved on wetting.

8. A soil colloidal particle may lose water upon heating even beyond the temperature at which there is no heat of wetting.

REFERENCES

(1) Baver, L. D., and Horner, Glen M. 1933 Water content of soil colloids as related to their chemical composition. *Soil Sci.* 36: 329–353.

(2) Mitscherlich, A. 1901 Untersuchungen über die physikalischen Bodeneigenschaften. *Landw. Jahrb.* 30: 361–445.

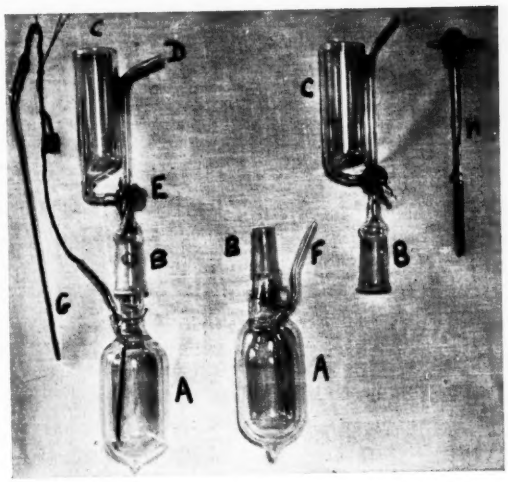
(3) Muntz, A., and Gaudechon, H. 1910 Les dégagements de chaleur qui se produisent au contact de la terre seche et de l'eau. *Ann. Sci. Agron. Franc. et Étrang.* 2: 393–443.

(4) PATRICK, W. A., AND GRIMM, F. V. 1921 Heat of wetting of silica gel. *Jour. Amer. Chem. Soc.* 43: 2144–2150.
(5) POUILLET, C. S. M. 1822 Sur les nouveaux phenomenes de production de chaleur. *Ann. Chim. et Phys.* 20: 141–162.
(6) Smithsonian Physical Tables 1933 Smithsn. Inst.
(7) WASHINGTON, HENRY S. 1930 The Chemical Analysis of Rocks. New York.

PLATE 1

CALORIMETER USED IN DETERMINATION OF HEAT OF WETTING

A, Wetting chamber; *B*, Ground glass joint; *C*, Reservoir; *D*, Airline; *E*, 3-way stopcock; *F*, Thin-walled glass tube; *G*, Thermoelement; *H*, Heater.


C
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A METHOD OF MEASURING THE CAPILLARY TENSION OF SOIL MOISTURE OVER A WIDE MOISTURE RANGE

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The ability of soil to retain water as soil moisture is a fundamental soil property. Because of the attraction of soil particles for water, they will hold a film of moisture against strong opposing forces. At any point below saturation, soil moisture is under a tension analogous to the tension in a liquid held by capillarity in a tube. This capillary tension increases from zero in completely saturated soil to a very high value in air-dry soil. If a water table stands below the soil surface, the tension at any point within the liquid per unit cross section at equilibrium is equal to the weight of a column of water of unit cross section and as high as the distance from the water table to the point. Since the weight of a cubic centimeter of water is 1 gm., the capillary tension in grams at any point above the water table at equilibrium is numerically equal to the height in centimeters from the water table to the point in question. It is convenient, therefore, to measure capillary tension in terms of grams per square centimeter or in centimeters of water.

As a soil passes from a wet to a dry state, greater energy is necessary to extract each succeeding unit of water, just as more energy is required to pump water from a well as the water becomes lower. This is true of all soils, but the amount of moisture soils will hold at any definite capillary tension is different for different soils and depends on the texture, structure, and composition. A measure of the moisture-holding power over a range of capillary tension not only furnishes a measure of the capacity of the soil for water storage but gives an index to the physical properties of the soil.

The use of capillary tension measurements by soil investigators has been restricted in the past by the lack of adequate methods of making these measurements. Various methods suitable for giving measurements over restricted ranges of moisture have been devised, and wide use has been made of the single value soil constants which correspond roughly to points on the curve. Thomas (6, 7) and others have contributed much information on moisture retaining power of soils in the drier range through vapor pressure studies, and Gardner (2), Richards (3), Richards and Gardner (4), and others have measured the region below one atmosphere tension by use of the capillary potentiometer or tensimeter. Little progress has been made in studying the range between one atmosphere and the range roughly corresponding to the wilting coefficient

where vapor pressure measurements become difficult, and until recently few attempts have been made to interpolate between capillary tensimeter and vapor pressure data to obtain a complete curve. Schofield (5) recently has taken data from several sources covering a wide moisture range, calculated these data in terms of capillary potential, and plotted the logarithms of the values obtained against the percentage of moisture. For convenience, and because the logarithm of the capillary potential is somewhat analogous to the negative logarithm of the hydrogen-ion concentration, he has adopted a similar type of symbol and termed the logarithm of the capillary potential pF.[1] This paper is a report of progress in the development of a method designed to give a measure of the complete range.

EXPERIMENTAL PROCEDURE

The method is based on the fact that if a sample of soil and some other material with power to absorb moisture are placed in contact, and one of the materials is moistened, water will pass from one to the other until equilibrium is approached. If the capillary tension curve has been determined for the absorbing material in contact with the soil, the tension for the soil is readily found by reference to the curve. Filter paper was found to be a suitable material for this purpose.

After a curve has been determined for the filter paper, the method is neither complicated nor difficult. Enough soil to fill a 10 cm. petri dish is made up to approximately the desired moisture content. One-third of this is placed in a smooth layer in the dish and covered with a dry 9-cm. filter paper. This is covered with another one-third of the soil. A wet filter paper is then placed on this layer and covered with the rest of the soil. The cover is then placed on the dish and the dish stored for 5 or 6 days in a closed vessel at approximately 25°C. At the end of this period the papers are removed from the dishes with a small amount of adhering soil which cannot be easily and quickly brushed off and are placed in separate tared weighing bottles and weighed. After drying at 110°C. for about 2 hours, the bottle and contents are again weighed to determine moisture loss. Moisture is determined also on a sample of soil from the petri dish.

To avoid decomposition of the paper by soil organisms, the filter papers are washed in 0.2 per cent $HgCl_2$ solution and dried before using. The dry weight of the paper is determined also before the soil moisture determination.

To calculate the percentage of moisture in the paper, the dry weight of the

[1] Schofield's symbol pF has not been adopted in this paper because of the possibilities of this symbol leading to confusion. The symbols pH and pOH are used to refer to the negative logarithms of ion concentrations. If the use of the symbol p in a similar connection is to be extended, it seems preferable to restrict its use to the concentration of ions, and pF would then refer to the negative logarithm of the fluorine-ion concentration. The substitution of some other letter in the place of p is suggested as a means of avoiding this possible confusion.

paper is subtracted from the combined dry weight of the paper and the adhering soil. This gives the dry weight of the adhering soil. To this dry weight is added the moisture which the soil contained before drying. This is determined from the moisture percentage found in the sample of soil taken for moisture determination. The wet weight of the adhering soil thus obtained, plus the dry weight of the paper, is then subtracted from the wet weight of the paper, plus wet soil. The result is the weight of moisture absorbed by the paper.

The moisture percentages found for the two papers are averaged, and the tension on the paper curve corresponding to this moisture is determined. The soil curve is then obtained by plotting this tension against the moisture found for the soil. Five or six points are sufficient for the plotting of a fairly complete curve.

Plotting the curve for the filter paper is a more difficult problem and involves using different methods for portions of the curve and combining the portions.

Little difficulty was found in obtaining the part of the curve below the wilting coefficient. For this part, papers were placed in desiccators over sulfuric acid of definite concentrations and left for several months in the dark at 25°C. after the desiccators had been evacuated. Both dry and wet papers were placed in the desiccators, and the average moisture percentage was taken. The paper which had been moistened was slightly higher in each case, but the difference was small. The data of Wilson (8) were used in determining the concentration of acid to use. Since each 0.0000171 mm. lowering of vapor pressure below the vapor pressure of water at 25°C. is equal to 1 gm. tension per square centimeter, the tension can be calculated readily from the vapor pressure lowering of the acid.

The curve covering the higher moisture concentrations was obtained by the use of a centrifuge and specially constructed tubes in the Trunion cups.

The relation of the capillary tension to the centrifugal force is given by the following equation:

$$\frac{d\psi}{dr} = r\omega^2 \qquad (A)$$

where ψ = capillary potential = capillary tension (numerically), r is the radius of the centrifuge to any point under consideration, and ω is the angular velocity. Integrating, we get:

$$\psi = \frac{r^2\omega^2}{2} - \psi_e \qquad (B)$$

in which ψ_e is the constant tension at the center of the centrifuge.

Taking two values of r and subtracting one equation from the other we get:

$$\psi_1 - \psi_2 = \frac{\omega^2}{2}(r_1^2 - r_2^2) \qquad (C)$$

Since the capillary tension is 0 at a free water surface, ψ_2 will be 0 if r_2 is at a water surface and the equation will be:

$$\psi = \frac{\omega}{2}(r_1^2 - r_2^2) \qquad (D)$$

which can be solved readily by substituting the proper values for ω, r_1, and r_2.

Special tubes were constructed for these determinations. They were made of brass tubing 3 cm. by 18 cm. with a solid partition soldered in 3 cm. from the bottom. The tubes were perforated 1 cm. above and just below the partition. This gave a small cup to hold water above the partition and allowed space below for water removed by centrifuging to collect. When centrifuging, water would not be thrown from the cup and would stand at the perforations. The tubes were filled to within 2 cm. of the top with quartz sand. This was covered with a muslin disc and a thin layer of soil to provide good contact, and the soil, in turn, was covered with a disc of filter paper. The paper to be tested was folded and placed on top of this. Stoppers were then inserted in the tubes to prevent evaporation.

The tubes were centrifuged for about 2 hours. Longer centrifuging did not materially change the results, but it is not probable that equilibrium was completely reached in this time. Further work will be necessary to establish this portion of the curve with precision.

DISCUSSION OF RESULTS

Experimental results of the method are illustrated in figures 1 and 2. Figure 1 is the capillary tension moisture curve for Schleicher and Shull No. 589 White Ribbon paper and is nearly the same curve obtained for other papers. The lowest four points on the curve should be comparatively accurate, since they are calculated from the average of wetting and drying papers which did not disagree materially. The upper portion of the curve is, no doubt, somewhat above the true value, as only drying papers were used. This would cause the absolute value of the soil curves derived from this curve to be too high also in this region, but would not change the relative values of the soil curves.

Figure 2 shows curves for four soils obtained by this method. Curves 1 and 2 are for sandy soils, curve 3 is for a loam, and curve 4 is for a clay loam. The papers were in contact with the soil only 4 hours in obtaining the fourth curve, and the dotted lines show the curves obtained from the wetting and drying papers separately. It is evident from these curves that equilibrium is reached very slowly even though the moisture moves a very short distance. The curves were much closer at the end of a week but were never quite together.

Hygroscopic coefficients for nine soils were determined by the method of exposing soil samples to a saturated atmosphere for 24 hours. Capillary tension curves for the same soils were determined by the method described above. It was found that the log of the average tension corresponding to

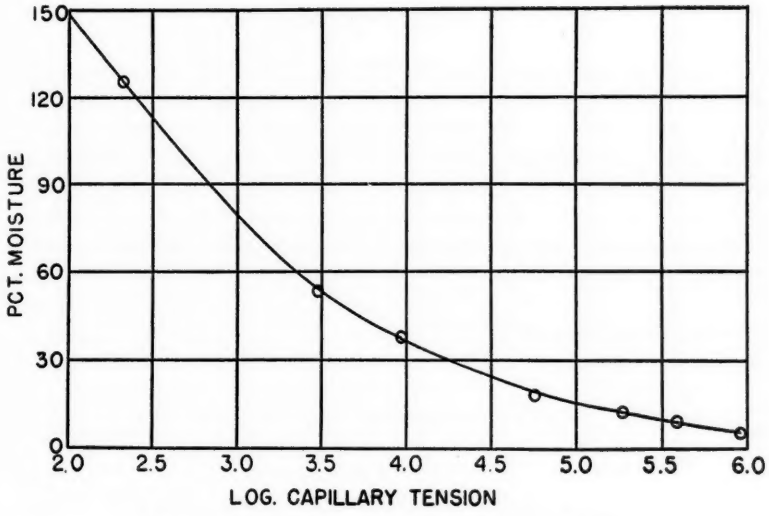

FIG. 1. CAPILLARY TENSION MOISTURE CURVE FOR PAPER

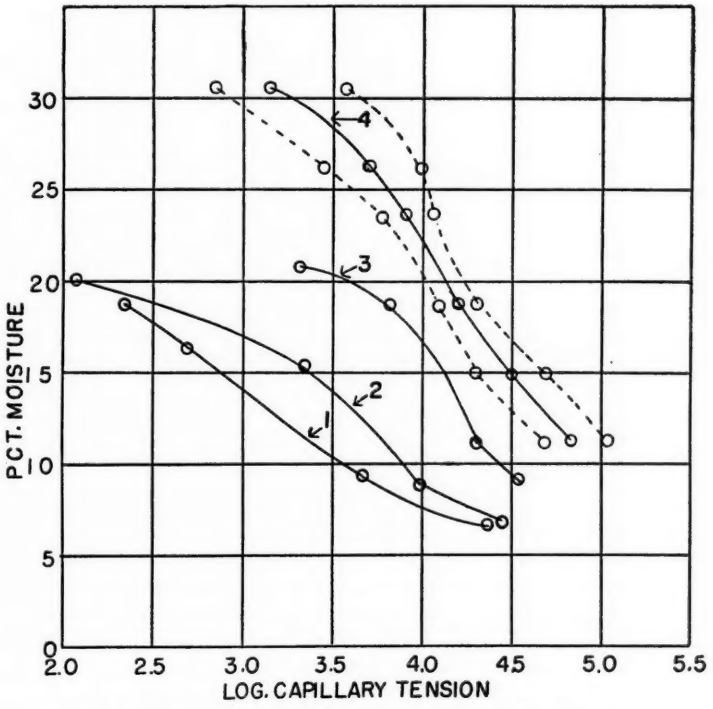

FIG. 2. CAPILLARY TENSION MOISTURE CURVES FOR FOUR SOILS

the hygroscopic coefficients was 4.71. The hygroscopic coefficients were then divided by the empirical factor 0.68 to obtain the wilting coefficients, and the wilting coefficients were multiplied by 1.84 to obtain the moisture equivalents. The tensions, expressed as grams, corresponding to these results are given in table 1; the averages are expressed also as atmospheres. The log of the tension at the average wilting coefficient is 4.1, which corresponds closely to Schofield's (5) figure of 4.2. The vapor pressure data of Thomas (6) indicate that the wilting coefficient is between 10 and 26 atmospheres. The average moisture equivalent was approximately 1 atmosphere. The factors 0.68 and 1.84 are from the data of Briggs and Shantz (1).

TABLE 1

Capillary tension at the wilting coefficient and moisture equivalent

SOIL NUMBER	CAPILLARY TENSION AT	
	Wilting coefficient	Moisture coefficient
	gm.	*gm.*
1	15,490	891
2	12,890	912
3	8,913	1,480
4	14,800	741
5	11,750	562
6	8,910	851
7	12,310	1,289
8	18,630	1,123
9	13,500	1,024
Average	13,021.4	985.9
Atmospheres	12.61	0.95

It would give these single value constants a greater fundamental meaning if they could be defined as the moisture content at definite capillary tension. Moisture tension curves should serve not only to improve the utility of the single value constants but to complete the information over the ranges between and beyond these constants.

SUMMARY

Progress on a new method of determining the capillary tension in soils has been reported.

The method consists of determining a capillary tension curve for a grade of filter paper and then indirectly determining the tension curve for soils by placing them in contact with the paper at various moisture concentrations.

Results show that capillary tension curves for soils may be determined by this method with sufficient precision to show the characteristic textural differences between soil types and may serve as a measure of moisture-storing capacity.

REFERENCES

(1) BRIGGS, L. J., AND SHANTZ, H. L. 1912 The wilting coefficient for different plants and its indirect determination. U. S. Dept. Agr. Bur. Plant Indus. Bul. 230.

(2) GARDNER, W. 1936 The rôle of the capillary potential in the dynamics of soil moisture. *Jour. Agr. Res.* 53: 57–60.

(3) RICHARDS, L. A. 1928 The usefulness of capillary potential to soil-moisture and plant investigators. *Jour. Agr. Res.* 37: 719–742.

(4) RICHARDS, L. A., AND GARDNER, W. 1936 Tensimeters for measuring the capillary tension of soil water. *Jour. Amer. Soc. Agron.* 28: 352–358.

(5) SCHOFIELD, R. K. 1935 The pF of water in soils. *Trans. Third Internatl. Cong. Soil Sci.* 2: 38–48.

(6) THOMAS, M. D. 1921 Aqueous vapor pressure of soils. *Soil Sci.* 11: 409–434.

(7) THOMAS, M. D. 1924 Aqueous vapor pressure of soils: II. Studies in dry soils. *Soil Sci.* 17: 1–18.

(8) WILSON, R. E. 1921 Humidity control by means of sulfuric acid solutions. *Indus. and Engin. Chem.* 13: 326–331.

ON THE MOBILITY OF EXCHANGEABLE CATIONS IN THE SOIL

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INTRODUCTION AND REVIEW OF LITERATURE

As a result of many studies of the soil replaceable complex, the composition and quantity of the exchangeable cations in various soils and their influence on the chemical, physical, and biological properties of the soil have been determined in many instances. The *quality* of the cations absorbed by the soil, however, has heretofore received much less consideration: all we know is that the absorbed cations are the most mobile, the most reactive part of the soil.[1] The question may be asked whether the reactivity of the absorbed cations, when they are desorbed or, in other words, their "mobility," is the same or different in different soils and different fractions of the absorbing complex of an individual soil.

It is difficult to find theoretical grounds for the assumption that absorbed cations in the soil's absorbing complex should be characterized by an identical mobility. Indeed, as the term itself shows, the absorbing "complex" of soil "is constituted of many separate chemical compounds" (Gedroiz). The mobility of the replaceable cations, bound with these compounds, must stand in a certain relation to their chemical nature, (e.g., depend on their content in organic matter, on the ratio $SiO_2:R_2O_3$) and to their physical properties. The composite character of the absorbing complex, and the multiplicity of its composition in different soils lead to the unavoidable conclusion that the exchangeable cations must possess a varying mobility both within the limits of one soil and in various soils.[2]

In spite of the obviousness of these statements, the problem of the mobility of the absorbed cations in soil has not as yet attracted the attention it deserves.

Only during the last decade, as the result of the unsuccessful development of the theory of soil acidity forms, was the question of the mobility of one of the absorbed cations in soil, hydrogen, investigated in detail. Studies made by Kappen and a number of other authors abroad and by Askinazi, Tiulin,

[1] Academician Gedroiz writes regarding this reactivity: "The soil absorbing complex approaches substances producing molecular and ion solutions in water, i.e., water-soluble soil compounds, and is the nearer to them, the higher the degree of its dispersion" (10).

[2] The lack of uniformity of the exchangeable cations within the same soil is proved, among other things, by the variability of the equilibrium "constants" in the equations of exchange adsorption in the soils. Compare, in this regard, our report to the International Conference of the Second Commission at Copenhagen in 1933 (13), and the reports by Fudge (7).

et al., in the U. S. S. R. show that the properties of the absorbed hydrogen ion in different soils, and even within the same soil, are not identical. According to location in the absorbing complex, a certain part of the exchangeable hydrogen is characterized by a high degree of mobility and another part, by a lower degree. The more mobile hydrogen ions are termed "exchangeable soil acidity," whereas the less mobile absorbed hydrogen ions are usually characterized as "hydrolytic soil acidity." According to Page (19), there is no fundamental difference between exchangeable and hydrolytic acidity. This viewpoint has been corroborated by Askinazi (2), who showed that absorbed H, of either the hydrolytic acidity of the soil or of the exchangeable acidity, may be replaced by cations of neutral salt. The only difference resolves itself into the time period of treating the soil with the salt solution. The less mobile hydrogen of hydrolytic acidity is displaced from the soil at a slower rate and with more difficulty by the cations of the neutral salt solution, than is the more mobile hydrogen of exchange acidity.

We shall abstain from dwelling on the vast literature devoted to the forms of soil acidity and shall indicate only that the numerous studies concerning this question indicate beyond dispute that the properties of absorbed hydrogen in soil (its mobility) vary continuously, depending on the character of the soil's colloids (acidoids), which dissociate the hydrogen ion.

The question of the mobility of the soil's absorbed bases was much less investigated up to the present.

Our knowledge of this question was limited to an understanding of the characteristics of the different exchangeable bases in respect to their energy of absorption. The question of the energy of absorption of the same exchangeable base in different soils, or within one soil, has scarcely been discussed in the literature. As a result the mobility of each of the absorbed bases, both within one soil and in different soils, was considered to be virtually the same.

The purpose of the present work is to raise the question of the mobility of absorbed bases, the facility of their displacement from soils, and to approach the solution by means of the literature available and of our own investigations on the desorption of cations from soils.

Of the work on the subject under discussion, without going into any details of the literature, the investigations of Parker and Pate (6), Vageler (7), Gedroiz (8), Jenny (9, 10), Cernescu (11), Wiegner (13), and Renold (12) should be noted.

Besides the investigations cited, the problem of the mobility and stability of the soil exchangeable cations in the complex has been touched upon in the studies of Chaminade (6), Fudge (7), Antipov-Karataev (1), Gorbunov (14), et al. The following conclusions may be drawn from all these studies: The mobility of exchangeable cations in different adsorbents is different, according to the physico-chemical properties of the adsorbents and the peculiarities of their structure; the mobility of exchangeable cations depends also on the degree of the saturation of the adsorbents with these cations.

In the present work the mobility of the absorbing cation was studied first in various soils saturated with one and the same cation; second, in one and the same soil saturated with various cations in various ratios. Twenty-six samples of various soils, collected by the U. S. S. R. Institute of Agricultural Soil-Science in the course of its agro-soil survey work for purposes of chemical manuring, were used for these experiments.

EXPERIMENTAL

Mobility of exchangeable cations in different soils of the U. S. S. R.

In order that the different saturation of the soils with the cations studied should not exert an influence on the results of the determinations, all soils experimented with were fully saturated with one cation—Ca or H.

For this purpose, the soils in one series of experiments were washed on a filter with 0.05*N* HCl until a complete displacement of Ca was achieved. In another series, they were washed with *N* $CaCl_2$ (pH = 6.2) until there was no observable acidulation of the outflowing filtrate.[3] In both cases, the excess reagent was washed away by distilled water until the filtrate ceased to react to chlorine. After this, the soils were brought to an air-dry condition by means of prolonged drying in the air at room temperature, and hygroscopic moisture was determined in the soil samples by drying at 105°C. to a constant weight.

The methods used for the determination of the mobility of soil exchangeable cations are generally similar to those used by Jenny for determining the "symmetry value." For the determination of the mobility of exchangeable calcium, weighed amounts of soils, saturated with enough calcium to contain 1 m.e. of exchangeable calcium, were shaken occasionally in the course of 48 hours with 200 cc. of 0.025*N* KCl. The relation between the amount of absorbed calcium in the soils and the initial amount of potassium in the solution (in m.e.) was maintained constant (1:5). The displaced Ca was determined in the filtrate by the volumetric method.

For determining the mobility of exchangeable hydrogen, weighed amounts of soils saturated with H, calculated so as to contain 1 m. e. of exchangeable hydrogen,[4] were shaken occasionally in the course of 48 hours with 100 cc. of 0.2*N* KCl (pH = 5.5). The relation of the amount of exchangeable H in the soils to the initial amount of potassium in the solution (in m.e.) was maintained constant (1:20). The amount of displaced H in the filtrate was determined by means of titration of the hot extract by alkali in the presence of phenolphthalein.

The mobility of absorbed Ca (or H) in the interaction of soil with KCl solutions was expressed by the quantity of displaced Ca (or H), in per cent,

[3] One l. of *N* $CaCl_2$ was used for washing 20 gm. of neutral soil.

[4] The content of exchangeable H in the soils saturated with hydrogen was considered equivalent to the absorption capacity of the soils studied, as determined by the method of Bobko and Askinazi (4).

of the original content of the cations of the soil sample. The results of the analyses are partially summed up in table 1. From the consideration of table 1 it may be gathered that the mobility of the exchangeable Ca and H is not identical in different soils, but changes according to the properties of the soils, in particular according to their content in organic matter. With the increase

TABLE 1

*Mobility of absorbed Ca and H in different soils (in their exchange with K)**

NUMBER	SOILS	ORIGIN	DEPTH	ABSORPTION CAPACITY PER 100 GM.	AMOUNT OF SOIL, SATURATED WITH H or Ca, TAKEN FOR THE DETERMINATION	MOBILITY OF EXCHANGEABLE H AMOUNT OF H DISPLACED FROM THE SOIL BY TREATMENT WITH 100 CC. 0.2 *N* KCl		MOBILITY OF EXCHANGEABLE Ca AMOUNT OF Ca DISPLACED FROM THE SOIL BY TREATMENT WITH 200 CC. 0.025 *N* KCl	
			cm.	*m.e.*	*gm.*	*m.e.*	*per cent*	*m.e.*	*per cent*
1	Humus-glei	Leningrad	2–10	8.8	11.4	0.26	26	0.23	23
2	Strongly podzolized turf	Moscow	3–10	7.4	13.5	0.19	19		
			140–148	15.1	6.6	0.38	38	0.37	37
3	Strongly podzolized forest soil	Western Region	7–14	8.1	12.4	0.42	42	0.51	51
			65–76	10.8	9.2	0.80	80	0.61	61
4	Mediumly podzolized	Western Region	2–10	4.5	22.2	0.34	34	0.24	24
			17–25	4.9	20.4	0.43	43	0.29	29
			100–110	8.1	12.3	0.68	68		
5	Weakly podzolized turf	Moscow	3–11	10.3	9.7	0.33	33		
			22–30	10.5	9.5	0.53	53	0.65	65
			127–137	19.6	5.0	0.67	67		
6	Gray-brown forest soil	Ural	0–8	32.6	3.1	0.43	43		
			40–48	34.4	2.9	0.79	79	0.65	65
7	Gray forest loam	Middle Volga	2–12	25.1	4.0	0.20	20		
			20–30	25.6	3.9	0.32	32	0.29	29
			120–130	18.1	5.5	0.54	54		
8	Loamy, weakly degraded chernozem	Middle Volga	16–26	51.9	1.9	0.30	30		
			110–120	36.7	2.7	0.51	51		
9	Leached chernozem	Glukhovo	2–10	19.8	5.1	0.30	30	0.44	44
10	Humus rich chernozem	Voronezh	2–10	52.6	1.9	0.30	30	0.40	40
11	Red soil (laterite type of soil formation)	Adjaristan	2–10	10.8	9.3	0.86	86	0.71	71

* The amount of exchangeable Ca or H in each soil was 1 m.e.

of the depth at which the sample was taken, and with the decrease of the percentage of organic matter in it, the mobility of the exchangeable cations Ca and H usually increases. In horizon A_0 of the investigated soils the least mobility of the exchangeable cations was observed in the chernozems; a medium mobility, in podzolized soils; and the highest, in red soils.

The following experiment was performed to determine to what extent the mobility of the exchangeable cations in different soils depends on their colloid composition, in particular, on their organic matter content. Humus-rich chernozem from Kamennaya Steppe, first saturated with hydrogen, was treated with 30 per cent H_2O_2 (Gedroiz method) until complete oxidation of the organic matter was achieved. According to Gedroiz (8) such treatment of soils with hydrogen peroxide destroys only their organic complex—"the mineral part of the soil remains with an undisturbed aluminum-silicate nucleus, i.e., in the same way as it was in the original soil."

Having isolated the mineral part of the chernozem of Kamennaya Steppe in the manner described, we hoped to approach the problem of the influence of the soil's organic matter on the strength of the bond between the exchangeable cations and the complex, by comparing the mobility of the exchangeable cations in the original chernozem and in its mineral part.

To elucidate this problem, samples of the original chernozem and of its mineral part were treated in one case with N $CaCl_2$ (pH = 5.5) until every discernible acidulation of the filtrate had ceased; and in another case, with 0.05N HCl, until the displacement of Ca and NH_4 was achieved.

TABLE 2

Mobility of exchangeable Ca and H in rich chernozem of Kamennaya Steppe and in its mineral part

	INITIAL CHERNOZEM	ITS MINERAL PART
	per cent	*per cent*
Mobility of exchangeable Ca	33	50
Mobility of exchangeable H	35	51

After the excess reagents were eliminated by washing with water, exchangeable Ca was determined in the samples. The content in exchangeable calcium was found to be in the original chernozem 47.5 m.e. per 100 gm., and in its mineral part, 28.55 m.e. per 100 gm. (or 23.4 m.e. per 100 gm. of the original soil). Thus in our case, the conclusion of Gedroiz (8) that in rich chernozems "half or more of the exchange capacity of these soils belongs to the organic part of the complex," was confirmed. The content in exchangeable H in the samples washed with HCl was considered equal to that of exchangeable Ca in the samples saturated with calcium.

Later, weighed soil samples, saturated with Ca, taken on the basis of 0.5 m.e. of exchangeable Ca (or H) were shaken occasionally in the course of two days in 100 cc. of 0.025N KCl or 0.2N HCl to determine the mobility of the exchangeable cations. The displaced Ca or H was determined in the filtrate, the latter by titration of the hot liquid in the presence of phenolphthalein. The results of the experiment are given in table 2.

Table 2 shows that after the oxidation of organic substances the mobility of exchangeable Ca, as well as that of H, in chernozem increases noticeably.

The influence of organic substance in soil evidently finds its expression in a decrease of the mobility of exchangeable Ca and H.

The differences in the mobility of the exchangeable cations in different soils can be explained, it seems, by the dissimilar structure of the atmosphere of absorbed cations in these soils.

According to Jenny, the absorbed cations are in continuous oscillating motion because of the Brownian and thermal mobility. The amplitude of these oscillations depends on the properties of the adsorbent and of the absorbed cations (their volume, valency, and other attributes). The oscillations of the exchangeable cations create on the surface of the adsorbent an *atmosphere of ions* (whether we ascribe the exchange capacity of soils to the double layer on the surface of soil colloids, or to the dissociation of the surface ions in the crystal lattice of the minerals). In soils with a high mobility of exchangeable cations, the atmosphere of ions has a loose structure.[5] Because of this the greater part of the exchangeable cations is involved in an interaction with the displacing agent. On the other hand, in soils with a low mobility of exchangeable cations, the atmosphere of cations, because of the chemical and other properties of soil colloids, has a compact structure. As a result, only a certain part of the exchangeable cations, chiefly those situated at the periphery of the ionic atmosphere,[6] enter into reaction with the displacing agent. The residual mass of exchangeable cations, which is more strongly bound with the complex, remains inert under these conditions. Similar results, in the sense of a different mobility of exchangeable cations in the permutite and clays, have been obtained by Wiegner (24). In his opinion "microns and ultramicrons have undulating contours in their external and internal surfaces"; in accordance with this "the diffused ionic layer possesses a variable surface similar to valleys, crevices, and channels; therefore the exchange reactions proceed with different intensities at different sites upon the external and internal surfaces of substance" (24). In adsorbents with an extramicellar exchange, which possess a less compact diffuse ionic layer, the mobility of the exchangeable cations must be higher; on the contrary, in adsorbents with an intramicellar exchange, which possess a more compact diffuse ionic layer, the exchangeable cations must possess a lesser mobility. Accordingly, in our experiments, the mineral soils (clays) with a prevalently extramicellar exchange were characterized generally by a higher mobility of the exchangeable Ca and H than was the soil rich in organic matter, in which the exchange proceeds mainly along the type of intramicellar reactions. The sharpness of these differences in the mobility of the exchangeable cations depends, of course, on the composition of the latter; as Wiegner says: "The differences in the strength of the bond of the ions will be greater if the ingoing ion is strongly hydrated and of a low valency, and the outgoing ion is the opposite of this" (24).

[5] The exchangeable cations possess a larger amplitude of oscillations according to Jenny (16).

[6] Those possessing a larger amplitude of oscillations, according to Jenny.

The mobility of exchangeable cations in different soils and the water properties of the latter

It is well known that the cations of salts in water solutions are to a greater or lesser degree subject to hydration processes because of the orienting of water dipoles around them. According to a number of authors (13, 23), absorbed cations in soil and other adsorbents are also surrounded by a hydrate envelope.

As the works of Janert (12) have demonstrated, in the course of the hydration of the absorbed cations in the soils, less heat of hydration is developed than in the case of the same cations existing there in a free state. In accordance with this observation the hydration of ions in a free, and in an adsorbed, condition apparently can not be regarded as identical; the adsorbed cations, situated in greater or less proximity to the negatively charged surface of the soil particles must, apparently, be surrounded by a lesser number of water dipoles than free cations in a solution. Proceeding from this idea, we may consider that the firmer the bond between the adsorbed cations and the soil complex, the less their hydration, as well as that of the anions of the inner layer (fig. 1); i.e., the less must be the hydration of the adsorbing complex, as a whole. This parallelism is noted also in the work of Wiegner (24), who says that the higher intensity of exchange in kaolin, as compared with permutite, correlates well with the higher water content of kaolin clays, as compared with permutite. The water of hydration of the soil exchangeable cations, as well as the water hydrating the inner layer of the double ion layer of the soil colloids, enters, as it is known, into the composition of the hygroscopic water of the soils. Therefore, the weaker the exchangeable cations bound with the absorbing complex of the soil (i.e., the higher their mobility), the higher must be the hygroscopicity of the soil, and vice versa. To verify this relation we compared the amounts of hygroscopic water in soils completely saturated with H or Ca (in millimols per milliequivalent of the exchangeable cations)[7] with the mobility of these cations in the same soils. The results of this comparison are shown in table 3.

The data summarized in table 3 indicate that the "hydration" of soils $\frac{(Hy)}{T}$ shows a general increase with the increasing mobility of the exchangeable cations, in accordance with the assumption made above. According to Behrens (3), the correlation coefficient between the mobility of exchangeable Ca in different soils and their hydration averaged 0.63 ± 0.16 for the 14 soils investigated; the correlation coefficient between the mobility of exchangeable H in different soils and their hydration averaged 0.88 ± 0.08 for the 26 investigated soils. The ratio of the heat of wetting to the heat of hydration of the cations saturating these soils also generally increased with the increase of the

[7] These quantities we designate in the following as "hydration" of the soil absorbing complex.

mobility of the exchangeable cations. The absence of strict correlation between the mobility of the exchangeable cations and the hydration of the soils is explained, apparently, by the presence of other forms of water in addition to water of hydration in air-dry soils, as well as by certain defects in the methods used by us for the determination of the mobility of soil exchangeable cations.

TABLE 3

*Relation between the mobility of absorbed Ca and H in different soils and the hydration of the soils**

NUMBER	SOILS	ORIGIN	HORIZON	AMOUNT OF ABSORBED CATIONS PER 100 GM. T	SOILS SATURATED WITH H			SOILS SATURATED WITH Ca		
					Hygroscopic water (millimols per 100 gm.)	Hy:T	Mobility of exchangeable H	Hygroscopic water (millimols per 100 gm.)	Hy:T	Mobility of exchangeable Ca
				m.e.	Hy		per cent	Hy		per cent
1	Humo-glei	Leningrad	2–10	8.8	79	9.0	26	114.0	13.0	23
2	Strongly podzolized turf	Moscow	3–11	7.4	55	7.5	19	.....	....	..
			140–148	15.1	125	8.3	3.8	.....	....	..
3	Weakly podzolized turf	Moscow	3–11	10.3	97	9.4	33	.....	....	..
			22–30	10.5	136	12.9	53	138.0	13.1	65
			103–137	19.6	289	14.7	67	.....	....	..
4	Gray-brown forest	Ural	0–8	32.6	261	8.0	43	.....	....	..
			40–48	34.4	419	12.2	56	38.3	11.1	65
5	Gray forest loam	Middle Volga	2–12	25.1	153	6.1	20	.....	....	..
			20–30	25.6	188	7.3	28	172.0	6.7	29
			120–130	18.1	189	10.4	54	.....	....	..
6	Loamy, weakly degraded chernozem	Middle Volga	16–26	51.9	367	7.1	30	.....	....	..
			110–120	36.7	381	10.4	51	.....	....	..
7	Leached chernozem	Glukhovo	2–10	19.8	156	7.8	30	199.0	10.0	44
8	Rich chernozem	Voronezh	2–10	52.6	366	7.0	30	485.0	9.0	40
9	Red Soil	Adjaristan	2–10	10.8	351	325.0	86	372.0	34.0	71

* By hydration of soils $\frac{Hy}{T}$, we mean the number of millimols of hygroscopic water (Hy) in the soils per m.e. of the absorbed cations (T).

The influence of the degree of saturation of the soil by cations on their mobility

The absorbing complex of natural soils is never saturated with only one exchangeable cation; in most cases the soil absorbing complex is essentially composed of at least two or three exchangeable cations, which satisfy most of the soil's exchange capacity. It will be demonstrated that the mobility of the exchangeable cations depends to a considerable degree on the composition of the exchangeable cations in the soil absorbing complex, and in particular on the degree of saturation of the soil by the exchangeable cation under consideration.

To explain the variation in the mobility of exchangeable cations at different

degrees of the saturation, let us consider the question of the distribution of two cations (one with a higher, the other with a lower energy of absorption) in the ionic atmosphere around a colloidal particle. Will the distribution of both cations in the ionic atmosphere be uniform, or will one of the cations concentrate in the layer immediately adjacent to the colloidal particle while the other cation concentrates in the external part of the atmosphere?

Theoretically speaking, one can scarcely expect a perfectly uniform distribution of two exchangeable cations in the ionic atmosphere surrounding a colloidal particle. One should suppose, rather, that one of the exchangeable cations, characterized by a higher energy of absorption,[8] would concentrate on the surface of the particle; and the other cation, possessing a lower absorption energy,[9] would concentrate at a greater distance from the surface of the absorbent.

It follows from the above discussion that if the complex contains different quantities of two cations, possessing different absorption energies, the mobility of the cation with the higher absorption energy should increase as the complex becomes saturated with it. Under these conditions the protective ionic layer with a lower energy of absorption, found in the periphery of the ionic atmosphere, will decrease. On the other hand, if the saturation of the soil by the cation with a higher absorption energy is decreased, its mobility must likewise decrease, since under these conditions the cations of low absorption energy occupying the periphery of the ionic atmosphere will be involved in the exchange. As to the cation with a lower energy of absorption, the decrease of the soil's saturation by it will not be accompanied by such a drastic drop in its mobility, since even at a low saturation of the soil by it, the cation with a lower absorption energy will remain *at the periphery* of the ionic atmosphere; in the case of an increased saturation of the soil with them even a decrease in its mobility is possible, since the cation of lower absorption energy will in this case occupy not only the peripheral layers of the ionic atmosphere, but will enter into the layers of ions located deeper,[10] i.e. closer to the surface of the colloid. The following experiments were arranged for testing the truth of these considerations.

Samples of degraded chernozem from the Shatilovo agricultural experiment station (almost entirely saturated by Ca and Mg), were shaken with 0.05*N* HCl; sample 1, once; sample 2, twice; sample 3, three times; and sample 4, four times.[11]

[8] By a lesser amplitude of oscillations, according to Jenny.

[9] A larger amplitude of oscillations, according to Jenny.

[10] This decrease of mobility will find, however, an obstacle in the law of mass action, according to which the mobility of exchangeable cations generally increases with the increase of the soil's saturation by them.

[11] After the soil was shaken with HCl for the first time, the solution was filtered and the soil washed off the filter into a flask, in which it was shaken with a fresh HCl solution for the second time; the following shakings were arranged in a similar way.

After HCl was removed by washing the soil with distilled water, and after the soil was brought to an air-dry condition, the exchange acidity of the samples was determined. For this purpose the weighed samples of the soils were washed with N $BaCl_2$ (pH = 6.2) until the filtrate was no longer acid. The extract was titrated against alkali in the presence of phenolphthalein. Equal portions of the samples (nos. 1, 2, 3, 4) were then shaken occasionally in the course of 48 hours with 0.2N KCl, 25 parts of the solution being added to one part of soil. The acidity of the filtrate was determined by repeated titration of the boiling solution against alkali in the presence of phenolphthalein. The results of these determinations are summarized in table 4.

From table 4 it is apparent that with the entrance of a small number of H ions into the absorption complex of the Shatilovo chernozem the mobility of the entering H is at its lowest. For instance, with the entrance of 5.83 m.e. H, only 6.6 per cent of it is replaced by a 0.2N KCl. As more of the H ions

TABLE 4

Mobility of absorbed H in samples of Shatilovo chernozem, saturated to a varying degree by H and Ca + Mg (in its interaction with KCl)

SAMPLE NUMBER	EXCHANGEABLE ACIDITY		H ION DISPLACED FROM SOIL BY SHAKING WITH 0.2 N KCl	
	Total	Per cent of capacity	Quantity	Per cent of the total exchangeable acidity
	*m.e.**	*per cent*	*m.e.**	*per cent*
1	5.83	16	0.39	6.6
2	14.30	39	1.37	9.6
3	22.84	62	5.70	24.9
4	27.96	76	11.12	39.8

* Per 100 gm. of soil.

enter the complex their mobility increases. For instance, with 27.96 m.e. of H, 39.8 per cent of the absorbed H was replaced by 0.2N KCl. The experiment described above shows that different forms of soil acidity, usually expressed by hydrolytic and exchange acidity, may also be applied to the exchange acidity itself. The mobility of H, corresponding to the exchange acidity of the soil, is not the same throughout; the highest mobility is possessed by those fractions of absorbed H, which replace the last traces of absorbed bases remaining in the soil.

Having demonstrated the varying mobility of adsorbed H, depending on the degree of saturation of the soil with this cation, let us proceed to the description of other experiments, showing a varying mobility of absorbed *bases* in the soil.

Samples of deep chernozem from the Kamennaya Steppe experiment station were shaken with 0.5N NH_4Cl; sample 1, once; sample 2, twice; sample 4, four times. Sample 5 was washed with 0.5N NH_4Cl on a filter until most of

absorbed Ca was replaced. The excess of NH_4Cl was removed from the soil by washing with ethyl alcohol. The completeness of the removal was established by the absence of Cl in the washings. After the soil was air-dried, absorbed Ca and NH_4 were determined in the samples. Equal weights of the obtained samples were shaken occasionally in the course of 48 hours with *N* KCl (1 part of soil in 25 parts of the solution), and Ca and NH_4 displaced from their absorbed condition were determined in the filtrate. The results of the determinations of Ca are given in table 5.

It is evident from table 5 that with the decrease of the soil's saturation with Ca the mobility of this cation, remaining in the soil in an absorbed condition, decreases; a 0.1*N* solution of KCl displaces 51.3 per cent of absorbed Ca from the original (i.e. untreated by NH_4Cl) chernozem. After most of the absorbed Ca has been displaced from the soil by treatment with NH_4Cl, the same KCl solution is able to displace only 16 per cent of the absorbed Ca remaining in the soil.

TABLE 5

Mobility of absorbed Ca in samples of chernozem from the Kamennaya Steppe Experiment Station, saturated to a varying degree by Ca and NH_4 (in their interaction with KCl)

SAMPLE NUMBER	ABSORBED Ca		ABSORBED Ca, REPLACED FROM SOIL BY TREATMENT WITH 0.1 *N* KCl	
	Total	Per cent capacity	Quantity	Per cent of initial content Ca in soil
	*m.e.**	*per cent*	*m.e.**	*per cent*
5	3.75	7	0.6	16.0
4	8.8	17	1.45	16.4
2	14.85	28	3.4	22.9
1	23.65	45	7.15	30.2
Original Soil	41.5	78	21.3	51.3

* Per 100 gm. of soil.

The result of the determinations of the mobility of absorbed NH_4 in the same experiment are summed up in table 6.

Table 6 shows that the influence of the degree of saturation of the soil by exchangeable NH_4 on the mobility of ammonium as a whole does not follow the rule established above for the mobility of exchangeable Ca and H; with the increase of the saturation of the soil by ammonium, in combination with Ca, the mobility of absorbed NH_4 shows hardly any change.

In another experiment we studied the influence of the saturation of the soil by Ba and H on the mobility of these cations in their exchange with potassium. For this purpose samples of a humus-rich chernozem from Kamennaya Steppe, saturated to varying degrees with Ba and H, were shaken occasionally in the course of 48 hours with 100 cc. of 0.1*N* KCl. The displaced Ba and H were determined in the filtrate, the later by titrating the hot liquid against 0.02*N*

NaOH in the presence of phenolphthalein. We determined also the pH of the filtrate. The results of this experiment are summed up in table 7.

The data of table 7 show that the mobility of hydrogen is reduced in accordance with the law of mass action, with the decrease of the soil's degree of saturation with hydrogen; on the contrary, with the decrease of the soil's degree of saturation with barium, the mobility of the latter not only is not reduced,

TABLE 6

Mobility of absorbed NH_4 in samples of chernozem from the Kamennaya Steppe Experiment Station, saturated to a varying degree by Ca and NH_4 (in their interaction with KCl)*

SAMPLE NUMBER	ABSORBED NH_4		ABSORBED NH_4 DISPLACED FROM SOIL BY TREATMENT WITH 0.1 *N* KCl	
	Total	Per cent of capacity	Quantity	Per cent of initial content NH_4
	m.e.†	*per cent*	*m.e.*†	*per cent*
1	31.75	60	17.25	54.3
2	38.65	73	23.00	56.9
4	48.75	92	26.00	53.2

* Besides Ca and NH_4 the chernozem samples contained also a certain amount of exchangeable Mg.

† Per 100 gm. of soil.

TABLE 7

Determination of the mobility of the different fractions of exchangeable Ba and H in samples of Kamennaya Steppe chernozem

SAMPLE NUMBER	EXCH. Ba IN SOIL		EXCH. H IN SOIL		DISPLACED FROM SOIL BY 0.1 *N* KCl				pH of KCl EXTRACT
					Ba		H		
	Quantity	Per cent capacity	Quantity	Per cent capacity	Quantity	Per cent of total	Quantity	Per cent of total	
	*m.e.**	*per cent*	*m.e.**	*per cent*	*m.e.**	*per cent*	*m.e.**	*per cent*	
1	56.45	100	0.0	0	.....	....	0.0	....	6.5
2	54.7	98	1.75	2	21.35	39.0	0.0	....	6.5
3	52.4	94	4.05	6	21.05	40.2	0.0	....	6.2
4	48.75	87	7.70	13	.....	....	0.35	0.9	6.0
5	44.6	80	11.85	20	20.5	46.0	0.39	0.9	5.5
6	35.35	63	21.1	37	19.25	54.5	0.53	1.2	5.0
7	19.1	34	37.15	66	12.95	67.95	4.23	11.1	3.0

* Per 100 gm.

as one would expect from the law of mass action, but it rises. The rise in the mobility of exchangeable barium with the decrease of its content in the complex cannot be explained by the acidulation of the reaction after the soil's interaction with KCl alone, since the mobility of barium increases somewhat even if the reaction shifts to the acid side quite insignificantly (down to pH = 5.5—5.0).

In the following experiment, a sample of Kamennaya Steppe chernozem, treated with 0.025*N* HCl until all the absorbed bases were removed, and washed with water until the Cl was likewise removed, was saturated with varying proportions of Ba and Na (Ba $(OH)_2$ and NaOH), so that the total of the absorbed Ba + Na was in each case 32.7 m.e. per 100 gm. of soil. The exchange acidity of the soil used in this experiment was about 50 m.e. Five gram samples of soil saturated with varying quantities of Ba and Na were shaken with 100 cc. of 0.017*N* KCl, and replaceable Ba was determined in the filtrate. The results of this experiment are shown in table 8.

In this experiment with a varying saturation of the soil by Ba and Na, we see the opposite of the preceding one: the mobility of exchangeable Ba increased with the increase of its content in the soil absorbing complex.

The data summarized in tables 4–8 thus confirm the above considerations; they show that the influence of the degree of saturation of the soil by a cation

TABLE 8

Mobility of absorbed Ba in samples of chernozem from Kamennaya Steppe, saturated to a varying degree by Ba and Na (in their interaction with KCl)

SAMPLE NUMBER	ABSORBED Ba		ABSORBED Ba, DISPLACED FROM SOIL TREATMENT WITH 0.017 *N* KCl	
	Quantity	Per cent of capacity	Quantity	Per cent of total content of absorbed Ba in soil
	*m.e.**	*per cent*	*m.e.**	*per cent*
1	8.0	15	2.04	25.5
2	16.3	31	7.35	45.1
3	24.3	46	13.6	56.0
4	32.7	62	19.45	50.5

* Per 100 gm. of soil.

on its mobility depends on the energy of absorption of the cations saturating the soil absorbing complex. If the increase of the soil's saturation by the cation under study arises at the cost of the decrease of the content of other cations of a lower absorption energy in the soil absorbing complex, the mobility of the cation under study increases considerably with the saturation of the complex by it. If, however, the increase of the soil's saturation by the cation takes place at the cost of the decrease of the content in the complex of other exchangeable cations with a higher absorption energy, compared with that of the cation, the mobility of which we are studying, this mobility either decreases (in contradiction to the law of mass action) with the rising saturation of the soil by this cation, or increases relatively little.

It follows also from the above data that the mobility of the exchangeable cation in the soil must depend on the energy of absorption of the other exchangeable cations which are present in the absorbing complex of the same soil simultaneously with it. If exchangeable Ca is accompanied in the soil by

an absorbed cation, possessing a higher absorption energy (e.g., by H), the mobility of exchangeable Ca must be high; if the same exchangeable Ca is in the same soil accompanied by an absorbed cation with a lower absorption energy (e.g., by Na), the mobility of exchangeable Ca must be lowered. The following experiments were arranged for the verification of this assumption.

Kamennaya Steppe chernozem, treated with 0.05 *N* HCl until all the exchangeable bases were displaced, and washed with water until the disappearance of Cl, was saturated with various cations by adding the respective hydroxides until a neutral reaction was reached. The quantity of the following

TABLE 9

Influence of the composition of exchangeable cations in Kamennaya Steppe chernozem on the mobility of the absorbed cation

AMOUNT OF ABSORBED CATIONS IN SOIL SAMPLE	AMOUNT OF NH_4Cl ADDED	AMOUNT OF Ca DISPLACED FROM SOIL	
		Quantity	Per cent of total Ca contained in soil sample
	m.e.	*m.e.*	*per cent*
Ca 0.5 m.e. + H 0.5 m.e.	5.0	0.30	60
Ca 0.5 m.e. + Mg 0.5 m.e.	5.0	0.18	36
Ca 0.5 m.e. + Na 0.5 m.e.	5.0	0.09	19

TABLE 10

Influence of the composition of exchangeable cations in Kamennaya Steppe chernozem on the mobility of absorbed Ba

AMOUNT OF ABSORBED CATIONS IN SOIL SAMPLES	AMOUNT OF NH_4Cl added	AMOUNT OF Ba DISPLACED FROM SOIL	
		Quantity	Per cent of total Ba contained in soil sample
	m.e.	*m.e.*	*per cent*
Ba 0.5 m.e. + H 0.5 m.e.	5.0	0.275	55
Ba 0.5 m.e. + Ca 0.5 m.e.	5.0	0.175	35
Ba 0.5 m.e. + Na 0.5 m.e.	5.0	0.11	22

cations were used: (A) 50 per cent Ca + 50 per cent H; (B) 50 per cent Ca + 50 per cent Mg; (C) 50 per cent Ca + 50 per cent Na. The proportion of the weight of soil taken for this saturation to the volume of the solutions was 1.91 gm: 150 cc. After 48 hours of contact 50 cc. of NH_4Cl were added which resulted in 0.025 *N* solutions of NH_4Cl. After 48 hours of contact of the soils with NH_4Cl, the suspensions were filtered, and the Ca displaced from the soils was determined in the filtrate with the help of the volumetric method. The results of these determinations are given in table 9. Similar results were obtained in another experiment, similarly arranged (table 10).

It follows from tables 9 and 10 that the mobility of exchangeable cations in one and the same soil at equal saturation changes with the composition of the accompanying absorbed cations in the complex. Moreover, the greater the absorption energy of the accompanying cations, the higher is the mobility of the exchangeable cation under study.[12]

DISCUSSION OF THE RESULTS

The study of the mobility of soil exchangeable cations is of great importance in agronomics, since the mobility of exchangeable bases determines their availability to the plants; and the mobility of absorbed hydrogen, its harmful effect on plants. The experiments arranged by us show that the mobility of absorbed hydrogen and, consequently, its harmful effect on the plants increases with the increase of the soil's saturation by it. Apparently, in the case of a low saturation of the soil's absorbing complex by hydrogen ions, these ions are

TABLE 11

Mobility of exchangeable hydrogen in various soils and the yield of mustard

SOIL (H-SATURATED)	MOBILITY OF SOIL ABSORBED H IN EXCHANGE WITH K	YIELD OF MUSTARD (GREEN MASS ROOTS)
	per cent	*grams*
Sand (Prianishnikov solution culture)	..	18.5
Solution culture + Kam. Steppe chernozem	30	8.9
Solution culture + Glukhovo chernozem	30	9.1
Solution culture + podzolized soil from Western Region, horizon A	42	7.6
Solution culture + podzolized soil from Western Region, horizon B	53	2.2
Solution culture + Chakva red soil	86	0.8

in the deepest layers of the ion atmosphere, which are but little involved in the exchange reactions.[13] The hydrogen ions, forming part of these deeper layers and lying in the immediate vicinity of the negatively charged surface of the soil particle, are known under the name of "hydrolytic acidity." With the increase of the amount of exchangeable hydrogen in the absorbing complex, the hydrogen ion begins to occupy sites which lie at a greater distance from the surface of the absorbent.[14] Accordingly the bond between it and the complex becomes looser while its mobility rises (cf. table 4, 7).

In the case of an equal saturation of soils with hydrogen, the mobility of the hydrogen may vary with the peculiar characters of the absorbing complex

[12] The mobility of exchangeable cations depends also, as has been shown by Renold and Marschall, on the method of their introduction into the absorbing complex.

[13] Chemically speaking, this can be explained by the formation of very weakly dissociated soil acids.

[14] It displaces the bases from the stronger soil acidoids.

of the soil. The following pot-culture experiment was arranged for studying the relation between the mobility of exchangeable hydrogen in different soils and its harmful effect on plants. Quantities of various soils, completely saturated with hydrogen and containing equal amounts of exchangeable hydrogen (10 m.e. per pot) + Prianishnikov's nutrient mixture, were introduced into pots with 1 kgm. sand in each. The yields of mustard obtained in this experiment are given in table 11.

As one can see from these data the harmful effect of equal amounts of exchangeable hydrogen in different soils increased in proportion to the increase of the mobility of exchangeable hydrogen in these soils. Judging by the results described in the present work, the harmful effect of exchangeable acidity on the plants must be least in soils rich in organic matter, which are characterized by the lowest mobility of absorbed hydrogen.

The fact of the unequal mobility of exchangeable bases in different soils, revealed by the present work, leads us to think that the availability of these bases to the plant in different soil types must also be unequal. Particular significance, moreover, may be attached to the degree of the soil's saturation by one or the other exchangeable cation. The data obtained in the present work show that the availability of exchangeable Ca to the plants must decrease sharply if the saturation of the soil by it decreases as a result of the introduction of Na ion into the absorbing complex. The work of Joffe (17) and of Ratner (21) completely confirm this conclusion. The reduction of the soil's saturation with potassium as a result of the introduction of Ca ion into the absorbing complex, on the contrary, must not affect to any considerable extent the availability of exchangeable potassium to the plants, as this also follows from the considerations presented above. This conclusion has been corroborated by our pot-culture experiments.

The results of the present work indicate that the mobility of the exchangeable cations in soil is, moreover, one of the factors which determines the water and physical properties of soils. The looseness of the bond of soil exchangeable cations with the complex conditions the presence of a large amount of hydration water unavailable to the plants. At the same time, such a loose bond of the exchangeable cations with the complex insures a greater stability of soil colloids and thus injures the physical properties of the soils. On the contrary, if the bond between the complex and the exchangeable cations is stronger, their hydration decreases, with the result that the stability of the colloids is also decreased and the physical properties of the soil are improved. The good physical properties of chernozems, as compared with certain other soils also saturated with Ca, may be in a certain measure considered as depending on the strength of the bond between exchangeable Ca and the complex in chernozem soils. This strong bond appears to be the result of the presence of large amounts of organic matter in chernozem soils. If this is so, then after the destruction of organic matter in chernozem, its dispersion must rise. This assumption has, indeed, found its confirmation in one of Gedroiz's (8)

experiments, in which the dispersion of chernozem is sharply increased when the soils were saturated with either hydrogen or with Ca, after the soil's organic matter was destroyed.

The favorable effect of organic matter on the physical properties of soils, which is commonly explained by its "gluing" or "cementation" property, may be, it would seem, more fully understood if we take into account the strong bond between exchangeable cations (Ca and H) in the organic matter, and their low hydration.

CONCLUSIONS

Intensive and extensive study of the problem of the mobility of soil exchangeable cations and of the strength of their bond with the complex are needed if we wish to have light on some still obscure questions of the physics and chemistry of soil.

The mobility of exchangeable cations depends upon the physico-chemical properties of the adsorbents and their structural characteristics, determining the strength of the bond uniting the cations and participating in the exchange with the complex.

This mobility also depends upon the degree of saturation of the complex by the cation in question.

In soils completely saturated by one cation, the mobility of exchangeable cations varies two-to three-fold in dependence upon the properties of the soil. The highest mobility is shown by exchangeable cations in red soils; the lowest, in chernozem. As we proceed down the soil horizons in the chernozem and podzolized zones, the mobility of the cations increases, as a rule.

The unequal mobility of exchangeable cations in different soils seems to be due to differences in structure of the ion atmosphere of colloids in these soils. Only that part of the exchangeable cations (the proportions being different in different soils) which composes the looser, external part of the ionic atmosphere, participates essentially in the exchange reactions.

In the case of two cations present in a varying proportion in the complex of one soil and possessing different energies of absorption, the strength of the bond of one of them with the complex (the one with a higher energy of absorption) decreases with the increase of the saturation of the complex by it, and its mobility increases. The mobility of the cation of lower absorption energy changes relatively little with the increase of the saturation of the complex by it.

The mobility of exchangeable cations depends not only on the kind of soil and on the degree of saturation of the complex by them, but also on the kind of the exchangeable cations accompanying them in the soil.

It proved possible to state the existence of a correlation between the mobility of exchangeable cations in different soils (at a complete saturation of the complexes of different soils by the same cation) and the "hydration of the absorbing complex" of these soils. The hypotheses governing this correlation are considered.

The strength of the bond between the exchangeable cations and the complex in different soils, which determines the hydration of the absorbing complex, appears to be one of the factors on which the stability of soil colloids and the physical properties of soils in general depend. It is necessary to study the physical properties of soils from this point of view.

It is evident from the above that the strength of the bond and the mobility of exchangeable cations possess an actual significance for the solution of a number of problems of agronomy, such as the physical properties of soil, the availability of exchangeable cations to the plants, the availability of soil moisture to the plants, the interaction between soils and fertilizers, and the effectiveness of fertilizers.

REFERENCES

(1) ANTIPOV-KARATAEV, I. N., AND KRASIKOV, K. N. 1933 Application of the method of electrofiltration, electrodialysis, and electrolysis in soil analysis. Trans. Dokuchaev Soil Inst. Studies in Phys. Chem. Properties of Soils No. 8.

(2) ASKINAZI, D L. 1934 On the nature of soil acidity. *Chem. Soc. Agr.* [Russian] No. 2: 45–50.

(3) BEHRENS, W. U. 1932 Zur Feststellung von Korrelationen nach der Rangmethode. *Landw. Jahrb.* 72: 591–605.

(4) BOBKO, E. V., AND ASKINAZI, D. L. 1925 On the methods of determining the exchange capacity and unsaturation of soils. Trans. Sci. Inst. Fert. [Russian] No. 25.

(5) CERNESCU, N. C. 1933 Kationenumtausch und Struktur. Bucharest.

(6) CHAMINADE, R. 1934 The equilibria between the complex absorbents and soil solutions. *Ann. Agron.* 4: 626—636.

(7) FUDGE, J. F. 1935 Mathematical relations between total exchange capacity and absorption of ammonium and potassium by soils. *Soil Sci.* 40: 269–284.

(8) GEDROIZ, K. K. 1931 Effect of hydrogen peroxide on the soil. *Udobrenie i Urozhai* [Russian] No. 9: 814–827.

(9) GEDROIZ, K. K. 1931 Exchangeable cations in soil. II. Liming and the relation between the exchangeable calcium and magnesium. *Udobrenie i Urozhai* [Russian] No. 11–12: 1047–1058.

(10) GEDROIZ, K. K. 1932 Theory of the Absorptive Capacity of Soils. Moscow.

(11) GORBUNOV, N. T. 1933 Studies on the exchangeable cations in soils. *Gedroiz Inst. Fert. and Agro-Soil-Sci. and Agrotechnic* No. 2: 51–77.

(12) JANERT, H. 1934 Application of heat of wetting measurements to soil research problems. *Jour. Agr. Sci.* 24: 136–150.

(13) JARUSOV, S. S., AND DMITRIENKO, O. I. 1933 On the problem of the mobility of the absorbed cations in soils. Trans. Internatl. Conf. Second Comn., Soc. Soil Sci. Copenhagen (see also 1934 *Internatl. Bodenk. Gesell. Sowiet Sektion Moscow* A).

(14) JENNY, H. 1932 Studies of the mechanism of ionic exchange in colloidal aluminum silicates. *Jour. Phys. Chem.* 36: 2217–2258.

(15) JENNY, H., AND COWAN, E. W. 1933 Über die Bedeutung der im Boden adsorbierten Kationen für das Pflanzenwachstum. *Ztschr. Pflanzenernähr. Düngung u. Bodenk.* (A) 31: 57–67.

(16) JENNY, H., AND REITEMEIER, R. I. 1935 Ionic exchange in relation to the stability of colloidal systems. *Jour. Phys. Chem.* 39: 593–604.

(17) JOFFE, J. S. 1935 Behavior of replaceable cations in the soil and their availability. *Trans. Third Internatl. Cong. Soil Sci.* 1: 66–67.

(18) KÜHN, S. 1932 Über die Beziehung zwischen Hykroskopizität, absorbierten Basen und einigen physikalischen Eigenschaften bei Böden. *Ztschr. Pflanzenernähr, Düngung, u. Bodenk.* (A) 26: 357–370.

(19) PAGE, H. J. 1926 The nature of soil acidity. *Trans. Second Comn. Internatl. Soc. Soil Sci. Groningen* A: 232–244.

(20) PARKER, F. W., AND PATE, W. W. 1926 Base exchange in soil colloids and the availability of exchangeable calcium in different soils. *Jour. Amer. Soc. Agron.* 18: 470–482.

(21) RATNER, E. I. 1935 Influence of exchangeable sodium in the soil on its properties as a medium for plant growth. *Soil Sci.* 40: 459–471.

(22) RENOLD, A. 1935 Cation exchange in permutites, especially in hydrogen and heavy-metal permutites. *Kolloidchem. Beihefte* 43: 1–142.

(23) VAGELER, P. 1932 Der Kationen- und Wasserhaushalt der Mineralbodens. J. Springer, Berlin.

(24) WIEGNER, G. 1936 Ionenumtausch und Struktur. *Trans. Third Internatl. Cong. Soil Sci.* (1935) 3: 5–28.

STUDIES IN THE ELECTRODIALYSIS OF SOILS: I. ELECTRODIALYSIS BY THE ROTATING ELECTRODE

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The use of the rotating electrode in ordinary electro-analysis is well known (3). The advantage claimed for this type of electrode is that by causing it to rotate at a high speed, greater current intensity and higher voltage can be applied, with more rapid precipitation of the respective metals resulting. The principle of this form of electrode has never been applied to soil work. The present paper deals with the possibilities of determining exchangeable bases in soils with the help of a rotating anode.

DESCRIPTION OF THE ELECTRODE

The rotating electrode shown diagramatically in figure 1 is a modification of Puri's electrofiltration apparatus, described in an earlier publication (2). It consists of a perforated copper cone resting in a glass funnel. An ordinary filter paper (preferably Whatman 50) is used for holding the soil suspension.

The rotating anode is cone shaped and is made from a perforated sheet or gauze of gold or platinum. It is rotated at about 200 to 300 revolutions per minute. Currents as high as 0.5 ampere can be passed from a 220 volt circuit with a suitable sliding resistance. Currents higher than 0.5 ampere result in too much heating.

EXPERIMENTAL

To test the efficiency of the rotating electrode as compared with the stationary one, it was considered advisable to work under strictly controlled conditions in which the disturbing factors due to the amount and nature of the exchangeable bases were eliminated as far as possible. This was done with one type of soil (a black cotton soil of high base exchange capacity), from which all the exchangeable bases were first removed by leaching with 0.05 *N* HCl, followed by leaching with water. Samples with different exchangeable bases were then prepared from this soil by treatment with hydroxides, using 50 m.e. of alkali per 100 gm. of soil. This was the amount present in the original soil, which had a pH value equal to 8.2. In the preparation of Mg and Ca soils, the requisite amount of the respective hydroxides was weighed and shaken with the soil suspension with the minimum amount of water for six hours, after which it was dried, or directly transferred to the electrodialysis apparatus.

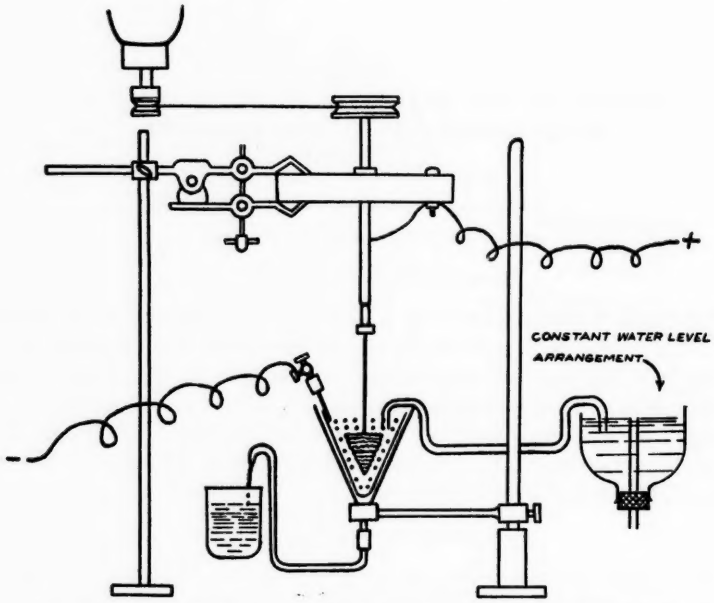

FIG. 1. DIAGRAM OF APPARATUS FOR THE ELECTRODIALYSIS OF SOILS BY THE ROTATING ELECTRODE

TABLE 1

Electrodialysis of single base soils with rotating anode (R. A.) and stationary anode (S. A.)
Current passed = 0.15 ampere

Series I. Gold disc-type anode (diameter 1.1″)

TYPE OF SOIL	TYPE OF ANODE	RECOVERY OF BASE DURING				TOTAL RECOVERY OF BASE IN 2 HOURS	TOTAL VOL. OF ELECTRO-DIALYSATE IN 2 HOURS	MAX. TEMP. DURING ELECTRO-DIALYSIS
		1st half hour	2nd half hour	3rd half hour	4th half hour			
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*cc.*	*degrees C.*
Na	R. A.	80.4	10.0	5.4	2.0	97.8	1346	48
	S. A.	42.0	11.0	10.4	9.4	72.8	1120	55
K	R. A.	60.4	13.2	6.6	4.4	84.6	1706	44
	S. A.	37.0	8.8	7.4	4.0	57.2	1569	47
Ca	R. A.	44.4	13.04	6.64	3.8	67.88	2093	41
	S. A.	21.0	2.64	1.44	1.24	26.32	2186	47
Mg	R. A.	9.0	2.8	1.8	0.8	14.4	1750	51
	S. A.	5.8	0.72	.....	Stopped after 1½ hrs.	6.52	1638	51

Five grams of soil was used in every case, and the current was maintained at 0.15 ampere in the first three series. The dialysate was titrated with standard acid after regular intervals of time, using phenolphthalein as indicator. Two

TABLE 2

Electrodialysis of single base soils with rotating anode (R. A.) and stationary anode (S. A.)
Current passed = 0.15 ampere

Series II. Disc shaped anode of platinum gauze (diameter 0.9″)

TYPE OF SOIL	TYPE OF ANODE	RECOVERY OF BASE DURING				TOTAL RECOVERY OF BASE IN 2 HOURS	TOTAL VOL. OF ELECTRO-DIALYSATE IN 2 HOURS	MAX. TEMP. DURING ELECTRO-DIALYSIS
		1st half hour	2nd half hour	3rd half hour	4th half hour			
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*cc.*	*degrees C.*
Na	R. A.	66.80	24.96	5.44	1.12	98.32	737	49
	S. A.	49.60	32.96	12.80	0.32	95.68	1249	47
K	R. A.	62.60	24.44	6.68	2.92	96.64	830	47
	S. A.	38.60	16.08	13.28	7.20	75.16	1419	49
Ca	R. A.	39.44	9.20	9.52	6.98	65.14	656	45
	S. A.	28.40	13.20	10.32	6.32	58.24	1183	45
Mg	R. A.	8.80	4.64	2.48	1.76	17.68	1168	54.5
	S. A.	7.92	3.60	2.40	1.60	15.52	1409	53

TABLE 3

Electrodialysis of single base soils with rotating anode (R. A.) and stationary anode (S. A.)
Current passed = 0.15 ampere

Series III. Cone shaped anode of platinum gauze (semi-circular piece of 1″ radius)

TYPE OF SOIL	TYPE OF ANODE	RECOVERY OF BASE DURING				TOTAL RECOVERY OF BASE IN 2 HOURS	TOTAL VOL. OF ELECTRO-DIALYSATE IN 2 HOURS	MAX. TEMP. DURING ELECTRO-DIALYSIS
		1st half hour	2nd half hour	3rd half hour	4th half hour			
		per cent	*per cent*	*per cent*	*per cent*	*per cent*	*cc.*	*degrees C.*
Na	R. A.	71.60	26.68	1.60	0.48	100.36	757	46
	S. A.	66.40	24.52	8.88	....	99.80	1085	51
K	R. A.	44.60	49.40	4.88	1.12	100.00	579	50
	S. A.	75.00	14.60	1.40	0.80	91.80	1076	50
Ca	R. A.	44.56	15.12	7.92	5.92	73.52	885	48
	S. A.	33.00	14.00	9.44	8.00	64.44	1134	51
Mg	R. A.	9.60	4.60	2.08	1.80	18.08	700	46
	S. A.	8.00	2.80	3.18	2.40	16.38	1508	49

types of anodes were used: perforated disc, and cone shaped, of various sizes. One was of gold, and the others were made from platinum gauze. The results given in tables 1 to 5 are expressed in percentages of the total base present in the soil.

In order to compare the rotating electrode with another standard type, Basu's electrodialysis apparatus (1) was used with the same single base soils. This apparatus was preferred for comparison as great rapidity is claimed for it. The results of this experiment are given in table 5. The following conclusions may be drawn from the results given in tables 1 to 5.

1. Electrodialysis, as revealed by the percentage recovery of exchangeable bases, is quicker with the rotating electrode than with the stationary one.

2. Different exchangeable bases take varying lengths of time for displacement by the same current density. The order of their ease of displacement is Na > K > Ca > Mg.

TABLE 4

Electrodialysis of single base soils with rotating anode (R. A.) Current passed = 0.5 ampere

Series IV. Cone shaped anode of platinum gauze (semi-circular piece of 2″ radius)

TYPE OF SOIL	RECOVERY OF BASE DURING				TOTAL RECOVERY OF BASE IN ONE HOUR	TOTAL VOL. OF ELECTRO-DIALYSATE IN ONE HOUR	MAX. TEMP. DURING ELECTRO-DIALYSIS
	1st 15 min.	2nd 15 min.	3rd 15 min.	4th 15 min.			
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*cc.*	*degrees C.*
Na	52.20	45.20	3.40	0.48	101.28	417	48.5
K	77.76	17.96	2.80	0.48	99.0	608	56
Ca	52.40	21.84	7.84	4.96	87.04	833	60
Mg	8.80	4.80	2.64	1.28	17.52	1130	67

TABLE 5

Electrodialysis of single base soils with Basu's Apparatus

Series V

TYPE OF SOIL	RECOVERY OF BASE DURING				TOTAL RECOVERY OF BASE IN 2 HOURS	TOTAL VOL. OF ELECTRO-DIALYSATE	TEMP. OF ANODE CHAMBER	TEMP. OF CATHODE CHAMBER
	1st half hour	2nd half hour	3rd half hour	4th half hour				
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*cc.*	*degrees C.*	*degrees C.*
Na	20.26	37.20	26.60	7.00	91.06	310	65.5	76.5
K	26.40	39.80	18.00	5.20	89.4	334	54	59
Ca	13.40	14.60	9.40	7.20	44.6	652	54	67
Mg	2.20	1.00	1.00	0.40	4.6	262	75	84.5

3. There is very slight recovery of Mg, and it is doubtful if the total content could be recovered by electrodialysis within a reasonable time.

4. The volume of the electrodialysate is slightly greater, and the maximum temperature of the anode chamber, slightly higher in the case of the stationary electrode than in the case of the rotating one.

5. Currents as high as 0.5 ampere can be passed, using the rotating electrode, without too much heating resulting. With this current exchangeable bases can be recovered in less than an hour.

6. The advantages of a rotating anode are greatly minimized when the size of the anode is large (series III).

In using Basu's apparatus it was found that a large quantity of the displaced Ca gets caught in the allundum thimble, resulting in a slow appearance of this base. Another defect observed in this apparatus, when a number of cells are used together, as in the final design recommended by the authors, is that since there is one rheostat to control the current it leads to unequal distribution of current density in the various cells. As a result there is too much heating in some cases, and very little current passing through in others.

It is worthy of note that a large proportion of the alkali in the dialysate may get converted into carbonate, or even bicarbonate. This tendency is greater after the electrodialysis has gone on for some time. This point will be examined in greater detail in a later publication. Another point which has not been recognized so far is the influence of the quality of water used for electrodialysis. It is well known that distilled water, unless stored in specially resistant glass, will dissolve appreciable amounts of alkali from the container. If this water is used, and the volume of the dialysate is as much as two liters, as frequently happens, it can introduce appreciable error in the results; especially if the total exchangeable bases in the soil are not high. It is therefore important that the water used for electrodialysis should be tested for alkalinity, and the volume of the dialysate kept as low as possible.

It has been shown that by use of the rotating electrode removal of the bases is effected in a very short time and, consequently, the volume of the dialysate is comparatively small.

The arrangement of apparatus suggested in this paper is simple and cheap. A number of electrodes could be run with the same motor. It is, however, necessary that each cell should have a separate rheostat to adjust the current, which can be kept at approximately 0.5 ampere.

Electrodialysis has limited value as a means of determining exchangeable bases, especially in the case of replaceable Mg; but the rotating electrode is a distinct improvement over the stationary one in regard to rapidity of displacement.

SUMMARY

An apparatus for the electrodialysis of soils with the rotating anode is described.

The rate of electrodialysis depends on the nature of the exchangeable base.

REFERENCES

(1) Basu, J. K. 1931 An electrodialysis apparatus for the determination of replaceable bases in soils. *Jour. Agr. Sci.* 21: 484–492.

(2) Puri, A. N. 1930 Electrofiltration: a new method of removing exchangeable bases from soil colloids. *Soil Sci.* 30: 413.

(3) Smith, E. F. 1918 Electro-Analysis, ed. 6, P. Blakiston's Son & Co., Philadelphia.

REPLACEABLE BASE DETERMINATION BY ELECTRO-MIGRATION[1]

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INTRODUCTION

In 1934, Wheeting (4) reported on an electro-migration method for replaceable base determination. Briefly, this method consists of causing the replaceable soil cations to migrate, under an electrical potential, through a column of agar in which the soil sample is embedded, into an agar section free of soil particles. Then, in the soil-free media, the replaced bases may be determined quantitatively by ordinary methods. A 2 per cent agar gel containing a colored and more slowly moving ion (0.5 *N* cobalt acetate) is placed on the anode side of the soil to serve as the electrolyte in place of the normal ammonium acetate used in the balance of the agar column. The cobalt also serves to indicate the migration velocity.

Partially because of the unique system employed our interest was aroused, and work was started to compare the method with the methods used by the Kansas Experiment Station. The initial work done was in almost exact accordance with the published procedure. However, the results obtained for replaceable calcium were about 60 per cent below values believed to be correct. This discrepancy served to intensify our interest in the method and the physico-chemical mechanism upon which it is based. Our investigation, which was started in June, 1934, was delayed by the burning of our chemistry building together with all equipment and assembled data.

The investigation here reported is a study of the method, rather than of a soil. Only replaceable calcium and magnesium have been determined, and but three soils have been studied. The results obtained were compared with three other methods of determining exchangeable bases. The location in the agar column of the replaced ions, and the mechanism of the system have received especial attention throughout the work.

EXPERIMENTAL

During the first series of tests of the migration method, it became evident that certain changes had to be made in the procedure as published. The potential indicated (110 volts) was not sufficient to produce either the specified

[1] Contribution No. 215 from the Department of Chemistry.

current intensity or migration time; hence it was increased to 200 volts, which was found adequate. It became imperative, possibly because of this increase, to place a cold water jacket about the migration tube to prevent liquefaction of the agar gel. When it appeared that a large percentage of the ions were not recovered in the analysis of the agar section from the cobalt boundary to the cathode end, the cobalt boundary was allowed to move about 2 cm. in advance of the soil section. Then to determine where, in the agar column, the replaced ions were deposited, the column was divided into the following sections for individual analysis: (*a*) from 2.2 cm. behind the cobalt edge to 1.2 cm. behind it; (*b, c, d, e, f*) successive 1-cm. sections; (*g*) the next 15-cm. section; and (*h*) the balance of the column. (See figure 1.)

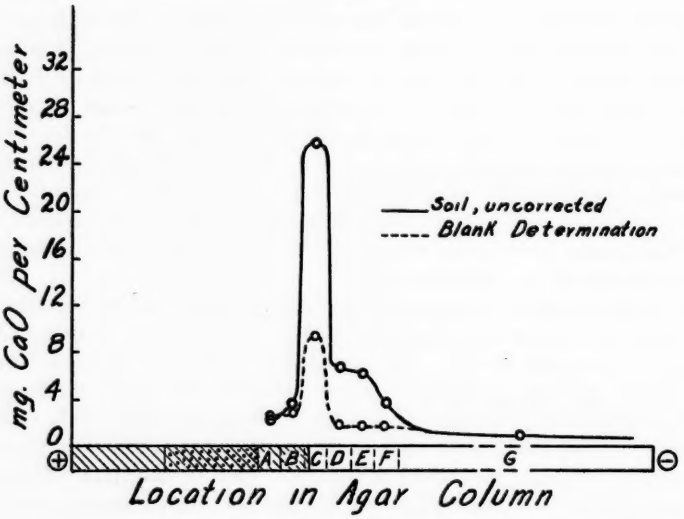

FIG. 1. DISTRIBUTION OF CALCIUM IN AGAR-AGAR COLUMN AFTER ELECTRO-MIGRATION
Cross-hatching represents 0.5 *N* cobalt acetate media; dots represent soil particles.

Since the agar used in the method contained very considerable quantities of all the ions being sought, it was necessary to obtain a blank determination. The suggested method was to analyze an agar section of the same size as that required for an unknown and to use values thus obtained as the correction. This method, however, proved to be of little value, for the ions in the agar were also replaceable. Consequently, a blank determination of the agar column was made, in every way identical to the soil determination, except that the soil itself was omitted or replaced by acid-washed, powdered silica. The section-by-section analysis of this "blank" column then gave the values to be deducted from the soil analyses.

The three methods of exchangeable base determination used to parallel the electro-migration method were:

1. The Gedroiz (3) 0.05 *N* HCl leaching method
2. Neutral normal ammonium chloride leaching (2)
3. Normal cobalt acetate leaching

The last method was used to see if a simple leaching process using cobalt acetate as the leaching agent would be as effective as the more elaborate electrical method. The method was as follows:

> Saturate 10 grams of the soil with 10 cc. of normal cobalt acetate solution and allow to stand for a short time. Filter, wash with four successive 5-cc. portions of the cobalt solution, wash with water until the filtrate is cobalt-free as shown by a basic sulfide test. The filtrate and washings are then analyzed by the usual methods.

Analytical procedure followed the A.O.A.C. methods (1) as far as possible. Agar sections were dried and ashed in quartz dishes. Cobalt, where present, was removed by an ammoniacal sulfide precipitation, which was shown by controls to be a safe procedure.

In addition to the chemical determinations designed to tell the quantity and location of the replaceable cations, a potential gradient investigation was made to explain why the ions were found where they were. For this purpose a special migration tube was prepared having along its length eight small side arms through which could be placed a pair of platinized platinum electrodes which were set in glass 1 mm. apart. To these were attached a potentiometer by means of which potential gradient determinations could be made. By placing the electrodes through the various openings while the tube was in operation a series of readings was obtained, and the potential gradient curve made. To investigate more closely the condition existing at the cobalt-ammonium boundary, further tests were made leaving the electrodes at one point in the agar column and allowing the cobalt boundary to move past it. In these measurements the electrodes usually developed a small galvanic potential, which must be deducted from the total measured effect to give the net gradient value. To determine the electrode potential, the tube power was momentarily removed after each potential measurement, and the correction reading was taken.

RESULTS

The most salient feature of the section-by-section analysis of the agar column after the migration process was completed was a decided concentration of replaced ions at, and just ahead of, the cobalt-ammonium acetate boundary (see fig. 1 and 2). In one typical case the 1-cm. section including the border yielded approximately 55 per cent of the total replaced calcium, whereas the successive 1-cm. sections contained 17, 14, 5, . . . per cent of the total. This boundary concentration was almost identical for both calcium and magnesium and extended as well to the blank determination.

Results of the analyses by the four methods of replaceable base determination were in fair agreement. The results compiled in table 1 are for a soil sample from a local fertility plot and are typical of all the soils studied.

Very significant in explaining the piling-up of the cations at the cobalt-ammonium juncture were the potential-gradient measurements. The cause for the observed concentration is an abrupt drop in the gradient or driving force occurring at the boundary. Figure 3, which is a composite curve made by the two methods indicated under "Experimental," shows the variation of potential gradient along the migration tube. It will be seen that the gradient

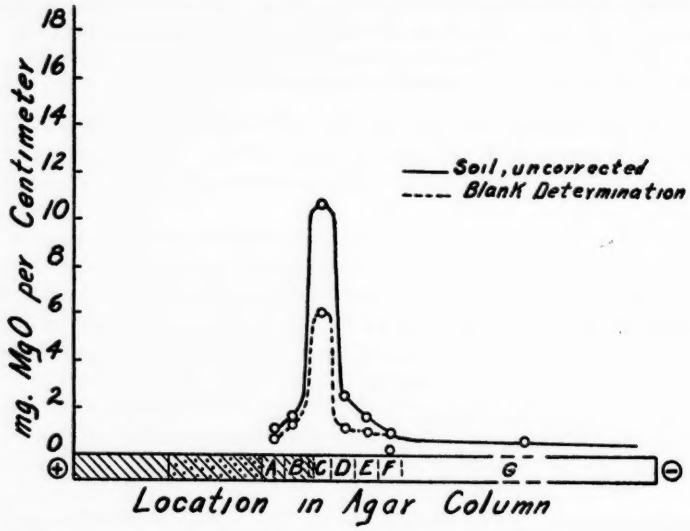

FIG. 2. DISTRIBUTION OF MAGNESIUM IN AGAR-AGAR COLUMN AFTER ELECTRO-MIGRATION
Cross-hatching represents 0.5 *N* cobalt acetate media; dots represent soil particles.

TABLE 1

Replaced soil cations by various methods, in milli-equivalents per 100 grams of soil

METHOD	CALCIUM	MAGNESIUM
I. Gedroiz, 0.05 *N* HCl leaching	11.6	3.88
II. Neutral, normal NH_4Cl leaching	10.7	3.68
III. Normal cobalt acetate leaching	11.1	3.73
IV. Electro-migration	9.7	3.76

in the ammonium section is about 30 per cent of that in the cobalt. The cobalt acetate section, being but 0.5 *N* and having a slower moving cation, presents a much greater electrical resistance than the normal ammonium acetate section. Hence, as the electrical resistance drops in going from the cobalt to the ammonium section, the potential gradient likewise diminishes in similar degree, and with it the migration velocity. From this it appears evident that, although the replaceable ions may be free to migrate at any time, their velocity

is low as long as they are within the ammonium acetate media. When the cobalt edge approaches the mobile ions, their velocity increases because of the increasing gradient. So, in effect, the cobalt edge pushes ahead of it the cations of the soil and agar and concentrates them in the boundary region where the sectional analysis reveals them. It should be further added that the sharp break in potential at the cobalt-ammonium interface migrates with the interface through the agar column. The observed potential increase occurring within the soil section (see fig. 3) coincides with that part in which a considerable portion of the electrolyte has been replaced by non-conducting soil particles. The lack of uniformity of this section is due to the settling of the heavier particles through the agar before it solidifies.

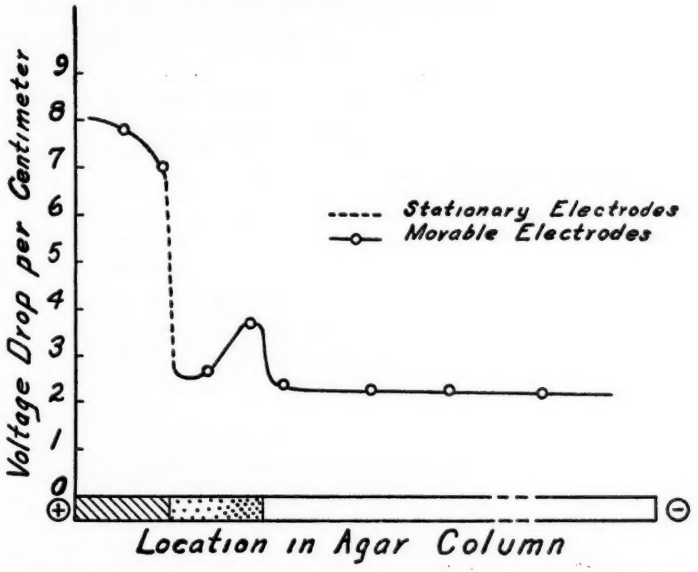

FIG. 3. CURVE SHOWING THE POTENTIAL GRADIENT IN THE AGAR-AGAR COLUMN AT START OF ELECTRO-MIGRATION

The major crest moves with the cobalt-ammonium interface across the column.

DISCUSSION

In the light of the sectional analyses, the low results obtained initially are explained. Since it was known that the migration velocity of calcium was high compared to cobalt, no great care was taken to include the cobalt-contaminated boundary section in the portion of agar to be analyzed. In this manner a high percentage of the cations were discarded prior to analysis.

Results obtained by the various methods indicate that all will give comparable values for calcium and magnesium. There has appeared no reason in this investigation why the mono-valent cations would act differently from

those studied. It is probable that the reported discrepancy in the mono-valent to di-valent base ratios obtained by the electro-migration and other methods should be sought in the proper application of the agar blank, since the agar is comparatively rich in the mono-valent ions.

The electro-migration method appears to the authors to be more complicated and subject to more variables and difficulties than a leaching process and, while capable of giving similar results, appears to have little decided advantage over a less elaborate system of replaceable base determination.

REFERENCES

(1) Association of Official Agricultural Chemists 1930 Official and Tentative Methods of Analysis of Official Agricultural Chemists. Washington, D. C.

(2) Gedroiz, K. K. 1918 Contributions to the method of determining zeolitic bases in the soil. *Zhur. O pyln. Agron.* [Russian] 19: 226. *Cited in Trans. Internatl. Soc. Soil Sci. Conf. Second Comn. vol. A.*

(3) Gedroiz, K. K. 1923 The hydrochloric acid method for determining in the soil the cations present in an absorbed condition. *Soil Sci.* 16: 473.

(4) Wheeting, Lawrence C. 1934 A migration method for the determination of replaceable bases in soils. *Soil Sci.* 37: 243–252.

BORON-DEFICIENCY EFFECTS SIMILAR IN GENERAL APPEARANCE TO BARK SYMPTOMS OF PSOROSIS IN CITRUS

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In the course of experiments in the nutrition of citrus (4) and (5) under controlled conditions, it was found that a boron deficiency produces characteristic symptoms in the leaves, twigs, trunk, and rootstock.

The experiments here reported do not deal with the problem of excessive boron but rather with that of a boron-deficiency. Boron was omitted from both sand and solution cultures until the initial symptoms of injury were visible. Boron in the form of boric acid (0.1 to 5 p.p.m.) was then supplied until recovery was evident, after which boron was again omitted. This alternation of a deficiency followed by an adequate supply of boron was continued until the effects after a recovery period were pronounced. In this way it was possible to note the permanent effects of previous periods of boron deficiency. There was a so-called building up of effects, both of injury and of recovery, with the trees gradually becoming larger, quite in contrast to the severe symptoms of injury that may be obtained, but with the death of the plant as a consequence.

When high concentrations of calcium were used in solutions supplied to sand cultures in which Washington Navel orange trees were grown, it was necessary to increase the concentration of boron to 1 p.p.m., or more, in order to prevent boron-deficiency symptoms. This may be the result of boron precipitation.

The method of preparing the culture solutions and of growing the citrus cuttings in solution cultures has already been described (3). The cuttings were grown in solutions in shallow enamelware pans of 8- to 21-quart capacity, and the budded trees were grown in silica sand in galvanized iron containers 20 inches in diameter and 24 inches deep.

Plate 1 shows one of a number of Valencia orange cuttings grown by Haas (3, pp. 484–485) in a culture solution containing 0.1 p.p.m. of manganese and of iron as tartrate. Boron was alternately omitted from the culture solution until injury was evident, after which 1 p.p.m. was supplied in order to bring about recovery. This type of boron treatment was carried on repeatedly. The photograph shown in plate 1 was taken during one of the recovery periods. The top of the cutting shows new growth in certain shoots while, in other shoots, all of the leaves have been lost. The root system apparently is in a

healthy condition. The trunk and branches, however, show the effects of the fluctuations in boron supplied to the culture solution.

Examination of the small twigs reveals numerous corky ridges in the bark as shown in plate 2. The largest branch in plate 2 is the same as the largest in plate 1. It possessed a smooth callused area that extended over much of the surface of the bark. The trunk of this cutting is seen in figure 1, plate 3. The upper portion of the trunk bears a callused bark wound while the lower portion shows the sloughing of bark as the callus forms underneath.

An interesting effect of a deficiency of boron was observed in budded orange trees (6 or more feet high) grown in solution cultures in 12-gallon earthenware jars. Two methods of creating a boron deficiency were used with effectiveness: (*a*) lengthening the period between changes of nutrient solution without the renewal of any of the constituents of the solution during the period, and (*b*) frequent renewal of the culture solution containing a deficiency of boron. By these means it was possible not only to produce the symptoms described by Haas and Klotz (5) but also to produce a splitting of the bark of the trunk and large branches in a direction parallel to that of their long axis. The wounds in some cases were 3 or more inches in length on branches 1 or more inches in diameter. The wood beneath the bark could be seen for the entire length of the wound. Within a few days after 5 p.p.m. of boron was added to the culture solutions in the jars (without the renewal of the old solutions) active callusing of the wounds was evident.

Another distinct and severe bark effect was produced with budded orange trees grown in sand cultures. These cultures received a solution lacking boron until injury was evident and then a solution containing 0.1 to 5 p.p.m. of boron until recovery was well under way, when boron was again omitted. This procedure was followed until a time during one of the recovery periods, when one of the trees was photographed. Figure 2, plate 3, shows the splitting of the bark and the callusing of the lesions. The outer layers of bark give rise to numerous scales.

There is a serious disease (psorosis) of orange trees in which numerous scales are associated with bark lesions (2). This disease has recently (1) been shown to be mosaic-like in nature and possibly of a virus origin. It is not to be confused with the physiological disease produced by fluctuations in the supply of boron in the present experiments.

In several sand cultures in which budded orange trees were grown, the culture solution was modified by increasing the concentration of calcium fourfold and by reducing potassium to one-fourth its usual concentration. In unpublished experiments, it was found that a greatly reduced potassium nutrition was accompanied by the production of gum pockets in the bark and exudations of gum in the leaves. When boron deficiency is complicated by a simultaneous potassium deficiency, the symptoms of boron deficiency seen in the bark are usually associated with gum exudations.

The experimental trees yielded too small a supply of bark material for the

chemical analyses desired. Because of the scaly condition of the bark of citrus trees affected with psorosis, it was considered excellent material in which to study in a preliminary way a few of the changes incurred. On October 28, 1935, collections of bark (psorosis-affected) from Washington Navel orange trees were made in a grove at Arlington, California, and collections of healthy bark from trees (considered as controls) in the field at the Citrus Experiment Station. A larger number of samples was desirable but was not available for control trees because of the large amount of bark necessary.

Boron determinations[1] of the dry bark samples showed 25, 31, 20, 28, 38, and 28 p.p.m. respectively for healthy trees and 22, 14, 20, 22, and 17 p.p.m. respectively for psorosis-affected trees. The percentages of calcium in the dry matter of the healthy bark samples were 4.74, 4.65, 4.30, and 4.28 while those for psorosis-affected bark samples were 5.06, 4.99, 5.40, 5.72, 5.22, and 6.37. The pectin contents calculated as percentages of calcium pectate in the dry matter were 25.83, 20.47, 19.55, and 19.16 for the healthy trees and 21.11, 18.64, 16.62, 16.28, 16.24, and 14.49 for the diseased trees.

These preliminary results obtained on bark from only two groves, and these several miles apart, are to be considered only as suggestive. As far as the data extend, they show that healthy bark contains a higher content of boron and pectin and a lower content of calcium than psorosis-affected bark. The higher calcium concentration of psorosis-affected bark might tend to lower the solubility of the lower boron content. It is possible that the infectious principle in some secondary way affects the boron content and that of other constituents. The continual loss of bark tissue in the form of scales may reduce the content of certain constituents.

It is well known, however, that psorosis affects citrus trees in districts in which excessive boron becomes a problem in the growth of the trees. No psorosis-like symptoms have thus far been obtained in artificial cultures with citrus by the use of excessive boron. These facts make it appear unlikely that boron is a factor in the causation of psorosis. It is of interest, nevertheless, that fluctuations in the supply of boron can produce bark lesions accompanied by callus production and scaling of the bark that imitate psorosis symptoms.

SUMMARY

Boron-deficiency effects that imitate bark symptoms of psorosis were produced in citrus.

Apparently the two diseases originate differently, but the effects may closely resemble one another.

REFERENCES

(1) FAWCETT, H. S. 1934 Is psorosis of citrus a virus disease? *Phytopath.* 24: 659–668.
(2) FAWCETT, H. S. 1936 Citrus Diseases and their Control, ed. 2, pp. 188, 371. McGraw-Hill Co., Inc., New York.

[1] The boron determinations here reported were made in collaboration with the Rubidoux Laboratory of the United States Department of Agriculture at Riverside, California.

(3) HAAS, A. R. C. 1932 Some nutritional aspects in mottle-leaf and other physiological diseases of citrus. *Hilgardia* 6: 484–559.
(4) HAAS, A. R. C., AND KLOTZ, L. J. 1931 Further evidence on the necessity of boron for health in citrus. *Bot. Gaz.* 92: 94–100.
(5) HAAS, A. R. C., AND KLOTZ, L. J. 1931 Some anatomical and physiological changes in citrus produced by boron deficiency. *Hilgardia* 5: 175–197.

PLATE 1

VALENCIA ORANGE CUTTING GROWN IN A CULTURE SOLUTION CONTAINING A FLUCTUATING BORON CONTENT

Boron was alternately omitted until injury occurred and then was supplied in concentrations of 1 p.p.m. until recovery set in. The loss of affected leaves, the scaly bark, and the excellent root system may be seen in this photograph, taken at the end of one of the recovery periods of growth.

PLATE 2

CORKY, RIDGED STRIATIONS ON THE SMALL TWIGS OF THE CUTTING SHOWN IN PLATE 1
At the right is a large lesion on a branch in which complete callusing has taken place.

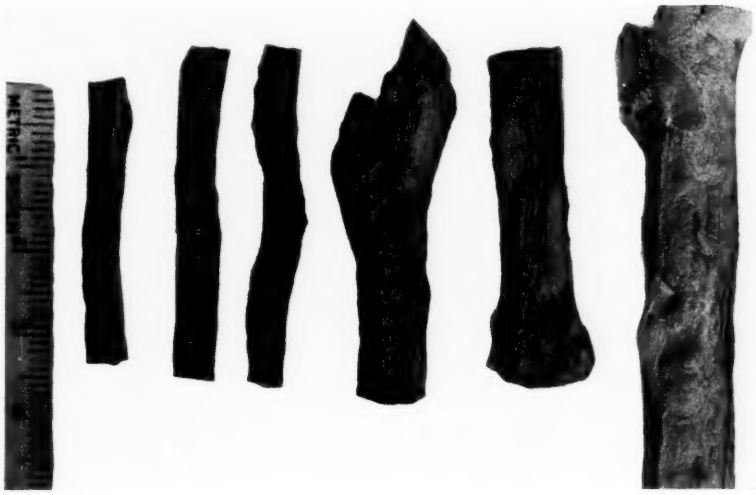
METRIC

PLATE 3

FIG. 1. Trunk of the cutting shown in Plate 1. The upper portion shows a large lesion fully callused; the lower portion shows the scaling of the bark as the callus forms.

FIG. 2. Budded orange tree grown in large sand cultures. Boron was alternately omitted until injury occurred, followed by the use of 0.1 to 5 p.p.m. of boron until recovery had taken place. The end of a recovery period, when the photograph was taken, was marked by severe scaling of the bark from the callused lesions.

FIG. 1

FIG. 2

THE DOCTRINE OF PLEOMORPHISM IN BACTERIOLOGY

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Pleomorphism of bacteria was born as a doctrine at the very dawn of bacteriological science. The literature will be reviewed, beginning with that early period, in order to show how this doctrine has developed and of what worth it is.

Following the morphological line of work initiated by Leeuwenhoek and extended by Ehrenberg, Ferdinand Cohn (5) devised his system of bacteria in 1872. He attempted to bring provisory order to an obscure domain and to expand it for intensive studies. In 1875 he defined his viewpoint as follows (6, p. 142):

. . . . innerhalb der Familie der Bakterien, glaubte ich eine grössere Zahl von Gattungen und Arten unterscheiden zu müssen, und obwohl ich mir nicht verhehlen konnte, dass es überaus schwierig sei, bei den Bakterien die Variationen, welche aus veränderter Ernährung oder anderen Lebensbedingungen hervorgehen, von den angeborenen und constant sich vererbenden Charakteren zu unterscheiden, so glaube ich doch, die von mir aufgestellten Abteilungen im Wesentlichen als natürlich ansprechen zu müssen.

The recognition that this group of elementary organisms is subject to botanical differentiation, as is every other group of cryptogams, was certainly a great achievement for that time. It was followed by studies executed chiefly by botanists (Brefeld, van Tieghem, Prazmowski), who described a number of well-characterized species of bacteria. Robert Koch, an early medical disciple of F. Cohn, applied his views to pathogens, with the brilliant success that is well known.

Cohn's system met immediately with sharp opposition. Billroth (3) tried to prove in a massive folio volume that all bacterial forms found in various putrefying substances belong to a certain pleomorphous *Coccobacteria septica*. Nägeli (12) thought that there was no reason for differentiating the thousands of bacterial forms he observed even into two species. Probably, he believed that the same species could provoke every kind of decomposition, every kind of fermentation, every kind of disease.

Extensive morphological studies on the group of the sulfur bacteria, which appeared at that time, took a position opposed to Cohn's views. This group of organisms with their conspicuous form, their abundant growth in sulfurous waters, and their peculiar characters, seemed a subject particularly favorable for morphological studies to verify F. Cohn's system.

Ray-Lankester (15) included all the varied forms found in sulfurous waters in the life cycle of a "protean" species because of their common red pigment, which he believed to be "the emblem of their common parentage, their race mark." Nevertheless he adds: "It is only if the possession of this purple colouring matter be admitted as warranting the assumption of specific continuity that my observations have any further interest."

Cohn (6, p. 157) rightly remarks upon this:

.... dass gerade diese Färbung irre leitet, da eine Anzahl mikroskopischer Organismen, welche meist gesellig unter einander vorkommen, aber durchaus nicht in entwickelungsgeschichtlichem Zusammenhang stehen, durch die nämliche Pfirsichblütfarbe charakterisiert sind.....

The objection had not prevented Warming (20) from falling into the same error. His observations on the same microflora, considered as a single species and called *Bacterium sulfuratum*, led him to the general conclusion, that the bacteria are "endowed with unlimited plasticity"; consequently, the system of Cohn and some other students who characterized genera and species according to their forms ought to be abandoned.

It is to the authority of the great botanist de Bary that we owe the clarification of all these misunderstandings and the application to bacteria of the generally accepted biological concepts of the differentiation of species, their characteristics, variability, and pleomorphism.

His *Vorlesungen über Baketerien* (2) had a profound influence on the sound development of bacterial researches, and it is regrettable that this exposition of the fundamental morphological problem and of the first principles of the morphological research method seems nearly forgotten by the younger generations of bacteriologists.

The writer, who greatly benefited by them fifty years ago, believes that the following quotations from Chapter IV (pp. 23–28) of these lectures could contribute to the elimination of misunderstandings which still persist:

.... kommen wir zu der viel diskutierten Frage, ob und wieweit es unter den Bakterien im Sinne der Naturbeschreibung *spezifisch* unterscheidbare Formen, *Species*, *Arten* giebt. Die Species werden unterschieden nach dem Entwicklungsgang. Die Gesamtheit der Einzelwesen und Generationen, welche während der zu Gebote stehenden Beobachtungszeit den gleichen, periodisch widerholten Entwicklungsgang—innerhalb empirisch bestimmter Variationsgrenzen—zeigen, nennt man Species. Wir beurteilen den Entwicklungsgang nach den successive in ihm auftretenden Gestaltungen. Diese bilden die Merkmale für die Erkennung und Unterscheidung der Species.....

Die Erfahrung hat gelehrt, dass verschiedene Species sich bezüglich der in ihrem Entwicklungsgang successive auftretenden Gestaltungen sehr ungleich verhalten können. Bei den einen kehren immer die gleichen successiven Gestaltungen mit relativ geringen individuellen Schwankungen oder Variationen wieder. Man kann sie *gleichförmige* Species nennen. Die meisten gewöhnlichen, höheren Pflanzen und Tiere sind Beispiele hierfür und nicht minder viele niedere, einfachere.

Die anderen Arten sind *vielgestaltig*, *pleomorph*, sie konnen selbst in den gleichnamigen Entwicklungsabschitten unter sehr ungleichen Gestalten auftreten, teils nach der Einwirkung

bekannter und experimentell willkürlich zu ändernder äusserer Ursachen, teils nach inneren Ursachen, welche der Analyse derzeit nicht zugänglich sind. . . . .

Für die Species der Bakterien sind nun zwei im Extrem sehr verschiedene Ansichten ausgesprochen worden. . . . .

Fortgesetzte Untersuchung hat nun schon jetzt, wie wohl behauptet werden darf, die Entscheidung geliefert und zwar dahin, dass es sich auf dem in Rede stehenden Gebiete mit den Species und ihrer Unterscheidung nicht anders verhalt als auf anderen Gebieten der Naturbeschreibung.

Die Species lassen sich unterscheiden, sobald man sorgfältig genug den Entwicklungsgang verfolgt. Manche der durch Brefeld, van Tieghem, Koch, Prazmowski näher bekannt gewordenen sind relativ gleichförmig; sie treten in den vegetativen Abschnitten der Entwicklung in der Regel in den gleichen Gestaltungs- oder Wuchs- und Gruppierungsformen auf. Andere sind in dieser Beziehung mannigfaltiger. . . . .

Eine grössere Vielgestaltigkeit kommt den höchstenwickelten Bakterienarten, Sphaerotilus, Crenothrix . . . . zu. Indessen handelt es sich auch hier nicht um Erscheinungen des eigentlichen Pleomorphismus, sondern nur um eine grössere Gliederung der aufeinanderfolgenden Stadien des Entwicklugsganges. Man wird eine Sonnenrose nicht deshalb pleomorph nennen, weil in ihrem natürlichen Entwicklungsgang Samenkorn, Keimpflanze, blühende und fruchttragende Pflanze nacheinander folgen. Vielmehr muss man daran festhalten, nur diejenigen Pflanzen als pleomorph zu bezeichnen, die . . . . in gleichnamigen Entwicklungsabschnitten unter sehr ungleichen Gestalten auftreten können.

Wer den einschlägigen Gegenständen und Untersuchungen ferner steht, wird nun fragen, wie es zu solch einschneidender Meinungsdifferenz wie zwischen Negation und Anerkennung von Species, kommen kann. Die Antwort lautet, dass die Differenz ihren Grund hat in Verschiedenheiten und auf der einen Seite in Fehlern der Untersuchungsmethode. Ich verstehe dabei unter *Methode* nicht, wie derzeit üblich, praktische Hand- und Kunstgriffe bei der Untersuchung, sondern den Gang der Fragestellung und der Beurtheilung der beobachteten Erscheinungen.

Die Species ist . . . . nur bestimmbar durch den und nur erkennbar an dem Entwicklungsgang und diesen besteht in der successiven Entwicklung von Formen, einer aus der anderen. Die später vorhandenen Formen entstehen aus den früheren, als *Teile dieser*, sie stehen daher mit denselben zu irgendeiner Zeit in lückenloser *Kontinuität*, auch wenn sie später von ihnen abgetrennt werden. Der Nachweis des Zusammengehörens in einen Entwicklungsgang kann daher nur erbracht werden durch den Nachweis dieser Kontinuität. Jeder andere Versuch, denselben zu erbringen, z. B. durch noch so sorgfältige Beobachtung an dem gleichen Orte nacheinander auftretender Formen, Konstruktion einer hypothetischen Entwicklungsreihe durch noch so genaue und geistreiche Vergleichung dieser, enthält einen logischen Fehler. . . . .

Diese Betrachtung klingt trivial; jeder wird sie für selbstverständlich halten, und sie ist es auch. Aber sie kann nicht oft genug wiederholt werden, denn gegen die Logik, welche sie veranschaulichen soll, wird fort und fort gesündigt, und eine Menge Konfusion verdankt diesen Verstössen ihre Entstehung. . . . .

The whole morphological problem in bacteriology could not have been better defined:

Bacteria, in spite of their elementary constitution, are, as other organisms, characterized by morphological types, that can and should be systematically grouped into genera and species.

The species can be determined only after establishing their evolution, that is, the successive forms arising one out of the other in a nearly constant order.

In characterizing a species allowance must be made for a certain degree of variation, also for a certain amount of individual fluctuation.

In these lines, written fifty years ago, the species controversy alone cannot awaken as keen interest as it did formerly; the other statements remain as vivid now as at the time they were made, especially the conception of pleomorphism.

That term is commonly used now in a sense that has little to do with its biological meaning as defined by de Bary. It means simply that a bacterium can be made to show more forms than it was originally noted to possess. A thesis opposed to evidence of this kind is commonly called *monomorphism*, a term coined much later, which sounds rather absurd, rigid uniformity being unthinkable in living organisms. However slight it may be, a succession of forms is always noticeable. This being so, any sharp morphological distinction between an evolution consisting of very few forms, and another composed of somewhat more of them, is hardly possible. The more so, since both are necessarily subject to variation and individual fluctuations. Obviously, both terms are lacking in clear biological conception and are applied in a rather lax, conventional manner.

The best way to get a clear idea of the problem is to follow the example of de Bary, putting bacteria aside for a time and considering the specific characters of higher organisms, plants in particular, where these characters are more conspicuous. Taking a sun flower as he does, or a wheat plant, or an oak tree, etc., we see that, in spite of their numerous stages of evolution and enormous rate of variation, they show a constant *biotype*, clearly recognized by the botanist, who will never be tempted to apply here the term of pleomorphism. There are other cases of organisms which show different and separate evolution cycles under seasonal and other influences, as in the classical case of Uredineae fungi. Such cases are still unknown among bacteria.

Resuming our history of the pleomorphistic doctrine, we come now to the papers by Zopf (26, 27), which attracted much attention among bacteriologists. The subject of his studies is again the group of sulfur bacteria, colorless and red. The author considers them as being vegetative forms of only two pleomorphous species of thread bacteria; he describes and illustrates their "progressive evolution" starting from the micrococcus stage, developing into short rods (bacterium) to long rods (bacillus), into long threads (leptothrix), into spirals (vibrio, spirillum, spirochaete); sometimes forming all kinds of zoögloeae with diversely grouped elements. Again the data are extended to be applied to the whole class of bacteria, and again the deficiencies of Cohn's system are emphasized.

Two years after the publication of Zopf's paper, the writer was studying the physiology of sulfur bacteria in de Bary's laboratory. He succeeded in discovering their peculiar energetics and then met with no difficulty in growing them in mass cultures and in drops of sulfur water under cover glasses (22). In the course of these researches, he grew familiar with their morphology and

thought it would be interesting to study it thoroughly. He wrote in 1888 (23, Introduction):

. . . . Vor Allem regte mich der diesen Organismen zugeschriebene exquisite Pleomorphismus dazu an, ihre verwickelten genetischen Beziehungen durch die Feststellung des Enwickelungsganges einzelner Formen klar zu legen, wodurch ich dem Wesen des Pleomorphismus bei den Bakterien überhaupt etwas näher zu treten hoffte. Auf die Genauigkeit und Sicherheit der Beobachtungmethode war in diesem schwierigen Falle besonders zu achten, und es hat sich gezeigt, dass ausschliesslich die continuirliche möglichst weit geführte Beobachtung des Entwicklungsganges einzelner Formen in mikroskopischen Kulturen hier zum Ziele führen kann. . . . .

By reason to their tendency to stick to glass, it was possible to follow the growth of isolated small groups of cells under the coverglass for days and weeks, by frequently renewing the sulfuretted mineral water, in which they were growing readily. Thus, groups of *Thiotrix* could be continuously observed for 56, 64, and 51 days, respectively; a single microcolony of *Thiocystis*, for 65 days; of *Lamprocytis*, for 60 and 20 days; of *Thiothece*, for 11 days; of *Thiodyction*, for 11 days, etc.

In this way Zopf's pleomorphous species resolved itself into a peculiar microflora classified into two genera of filamentous colorless sulfur bacteria and a dozen peach colored ones. His pleomorphism, though more moderate than the early one, proved again an error due to a faulty method, where the proof of continuity was totally lacking, replaced by "comparison of associated forms and construction of hypothetical evolution cycles"—after de Bary's apt expression. True, Zopf pretended to have made cultural experiments "in frischem Sumpfwasser," but this is a medium in which sulfur bacteria do not grow, which he did not know, since he knew nothing about the physiology of these organisms.

Summarizing his results, the writer went on to conclude (23, p. 115):

. . . . In der mehrfach erwähnten Untersuchung von Zopf haben, glaube ich, die auf ein enges Gebiet zurückgedrängten pleomorphistischen Anschauungen ihren letzten Widerhall gefunden. Sie müssen auch hier vor einer präciseren Fragestellung und genaueren Beobachtungmethode weichen. Die langwierige Controverse über die Bacterienspecies muss damit als endgiltig abgeschlossen betrachtet werden. . . . .

Indeed, for nearly 30 years, from 1888 to 1915, nothing more was heard of the doctrine of pleomorphism in spite of the most intense development of bacteriology in all of its branches. The ideas on bacterial morphology remained almost stable within the limits of the so-called Cohn-Koch thesis. This was due, perhaps, not so much to a correct biological conception of the characters of a species, as to the use of standardized culture media. Little wonder then, that with a steadily growing number of workers, applying different artifices of culture, aberrant forms of bacteria appeared, which puzzled the observers.

Without citing and separately criticizing the medical bacteriologists, gen-

erally held responsible for having brought forward pleomorphistic evidence, a general remark will suffice. The observations may be correct, but the interpretation given to the diverse forms observed cannot be taken seriously; they show nothing more than vague analogies with fungi, that surely every mycologist would hesistate to consider as established. In this kind of morphology imagination certainly plays a foremost part.

For several reasons the writer cannot forego a detailed criticism of the papers of Löhnis, et al. (9, 10, 11), on the life cycles of Azotobacter. The subject is one of the most important in the study of soil organisms; the work is of a very painstaking kind; the influence of these papers on recent Azotobacter studies is undeniable; finally, the errors committed present methodological interest. For, as will be seen, in this case the arbitrary interpretation is aggravated by gross material errors.

We will not recapitulate all the pretended Azotobacter transformations and regenerations in detail. The well known diagram (9, 11) showing four cycles at the four angles of the page, each containing many forms, joined by numerous lines and arrows with a central dark spot representing the *symplasm*, tells enough about the theory of life cycles. This symplasm is supposed to be a sort of central source of life of the organism, "all bacteria living *in vivo* as well as *in vitro* alternately in an organized and an amorphous stage." In the latter, all the forms are well melted and mixed together and then regenerate into various stages. Besides this general conjunction, there is another special one supposedly something akin to sexual conjunction. Five kinds of regeneration forms are described, a filterable stage, etc.

How do matters stand as to a method to prove such chaotic and highly improbable pleomorphism? Direct observation of the continuity of the stages of this truly protean organism is declared unnecessary. The correct application of the standard isolation and culture method would suffice to test the results claimed by the authors. Truly, the whole of a searcher's lifetime would hardly be sufficient to follow directly all of the transformations indicated by the arrows. Instead of that, Löhnis tried to enforce his arguments by means of an overwhelming mass of critical abstracts published in a volume in quarto, 250 pages with 18 plates with 89 figures, and 23 plates with 297 photographs, entitled "Studies upon the life cycles of the bacteria. Part I. Review of the literature 1838–1918." It is destined to prove that almost all the searchers actually observed pleomorphism, but were too blind to free their minds of the rule of the monomorphistic dogma. Justice must be rendered to the author for his painstaking bibliographic effort, but the work is by far not so profitable to students as it might have been, because of its immoderate bias.

More interesting are the errors mentioned, which should be discussed here in some detail. The source of them lies in the fact that the cultures of Azotobacter, isolated *lege artis* and qualified to be pure, become spontaneously impure with time. The cause of this annoying property is not difficult to

understand. It is due to a fundamental imperfection of the standard method of isolation by the plate technique. The method is reliable only in the case where the species to be dissociated grow almost equally well on the medium employed. As soon as there are any appreciable differences in the rates of colony formation, the isolation becomes less and less dependable, because of the presence of latent germs. The latter, when altogether unable to grow on the medium, render the success of the operation wholly uncertain. The case of the nitrifying bacteria, where isolation blunders occurred so often in the course of nearly fifty years, can be cited as one of the best examples of this uncertainty. Among many others, the example of Azotobacter is also one of the most instructive, for it is not difficult to detect all of the factors of its unreliability.

If an enrichment culture in Ashby medium is chosen for the isolation, as is commonly done, the operator has to deal with a mixture of Azotobacter and anaerobic spore formers. By plating, it seems easy to eliminate the latter, but even after repeated replating one can never be certain that these spores are entirely eliminated. Upon microscopic examination the material appears to be perfectly pure, good for inoculation on agar slopes; but there, with the Azotobacter slime growing abundantly on prolonged incubation, the few remaining spores can find sufficient protection from air to multiply, reproducing the original mixture of organisms.

If a more suitable method is used—silica jelly impregnated with ethanol or benzoate, sprinkled with earth particles for inoculation—the anaerobic spore formers do not appear, but there exists a group of minute bacteria—cocci and small rods not exceeding 0.5–0.6μ in size—which are regular messmates, or perhaps better called scavengers, of Azotobacter growth in soil and in cultures. Occasionally, annulated and branched rods which resemble Rhizobia are also found, sometimes curved vibrio-like short filaments. Evidently, they all obtain their nitrogen from the traces of ammonia which are liberated, and perhaps also live on the slime and substances produced from autolysis. Consequently, they cannot multiply in young Azotobacter growth, but persist in a quasi latent stage, till the aging of the culture brings about liberation of more ammonia and slime. It is possible to isolate them by adding small doses of ammonia to the agar or silica gel medium. One of them has been observed to produce a yellow pigment. Their growth is always exceedingly weak, the colonies seldom reaching 1 mm. in diameter; inoculation streaks grow as thin threads without spreading. Even in old Azotobacter cultures their growth is never abundant.

Unfortunately, Löhnis, instead of looking for some imperfection in his procedure, did not hesistate to include all of the impurities of his cultures in the life cycles of Azotobacter, in spite of a sharp dissimilarity of forms and a total absence of transition between them.

Finding a spore-forming bacillus in his "pure cultures" he immediately declares (10):

. . . . Es steht jetzt fest, dass in der That die grossen sporen-freien Azotobacter-Zellen Wuchsformen eines schlanken, Endosporen bildenden Bacillus sind. Bacillus Azotobacter ist demnach die korrekte Bezeichnung für diese Art. . . . .

In a joint paper with Smith (11), illustrated by seven plates of photographs, he describes and pictures as Azotobacter the very same tiny impurities before mentioned. They are seen perfectly reproduced on his plate C, photographs 13, 14, 15, 16, 17, and 18, and they are named, respectively, Azotobacter 24, Az.1, Az.15, Az.17, Az.17, and Az.7. The commonest of these impurities are the tiny coccobacteria of photographs 16 and 17; very common also is the coccus of photograph 13.

Again there seems hardly any possible doubt that the filterable stages which Löhnis and after him some other bacteriologists claim to have obtained are nothing but these tiny scavengers.

This behavior of Azotobacter cultures, becoming impure with age in spite of most careful purification, the writer has frequently had occasion to observe with his own cultures as well as with those obtained from abroad through the courtesy of fellow bacteriologists. Nearly 30 per cent of them, or even more, became impure, although there could be no possible doubt concerning the perfect execution of the standard operations.

Even 10 years ago, this cause of Löhnis' errors was evident to the writer, who wrote in his paper on nitrogen-fixing bacteria (24, p. 500):

. . . . Il est curieux que ce fait banal (pullulation tardive des impuretés) ait été le point de départ d'une théorie extravagante, dénuée de tout fondement expérimental, selon laquelle l'Azotobacter, et à sa suite les espèces bactériennes en général, passeraient par un cycle évolutif extrèmenent compliqué, comprenant une variété de formes.

The writer would have preferred to refrain from a thorough discussion of such a nearly evident error, but the appearance of a series of papers obviously inspired by Löhnis' suggestions made him change his mind. In fact, Niemeyer (13), Petschenko (14), Wilcke (21), Krassilnikov (8), de Regel (16), and Bachinskaya (1), made careful studies of the morphology of Azotobacter with the object of reproducing Löhnis' results under controlled conditions.

A detailed discussion of all the questions pertaining to Azotobacter morphology treated in these recent researches would require a special paper; only a brief summary of the principal points which they have in common will be given here.

All are agreed that the evolution of Azotobacter species under standard conditions follows a regular course: The young, motile cells take the shape of rods with rounded ends, which get shorter and more rounded with age, and pass into a coccus stage through repeated division, finally undergoing encapsulation; the last is the resting stage and the cells are termed cysts (or capsulated cells). There seems to be general agreement that this evolution is normal, not only in the recent papers, but also in the classical reports of Beijerinck, Omeliansky, and Prazmowski.

Besides the forms detected in the *normal course* of development, a great variety of aberrant forms have been noted; one part of them undoubtedly monstrous or undergoing manifest degeneration and autolysis, the other seemingly free from any such symptoms. An attempt is made to find a place for the latter in the morphological evolution of the organism, but there is much uncertainty about this point, and still more about the regeneration and reproductive forms. This uncertainty is due to the tendency and plan of these recent researches, devised under the influence of Löhnis' suggestions.

It was thought that the best way to bring about a maximum production of aberrant forms would be to use the largest possible number of differently composed media, and this was done with complete disregard of the mode of life of the species in its natural habitat. Thus, Petschenko used as many as 38 media; Batchinskaya was satisfied with 10, but among them were meat-peptone and bean decoction media to which Azotobacter is certainly not adapted. It was no wonder that this very sensitive soil organism reacted by producing a multitude of aberrant forms.

It is also possible that the organism was led to produce not only aberrant vegetative forms, but also abnormal regeneration forms, that were termed *regeneration units*, *gonidia*, and *arthrospores*. The description of these latter forms is far from clear. It would be a mistake to think that every mode of reproduction is normal and should be considered a regular stage in the development of the species. Again leaving bacteria for the moment, it is sufficient to recall the mode of reproduction of plants by slips or by grafts, which plays such an important part in horticulture, but which cannot be imagined as happening in nature, as it needs the artifices of the gardener. There is no reason for denying the likelihood of some unnatural happening in bacteriology: an aberrant mode of reproduction as a result of the artifices of the bacteriologist.

To sum up, the new pleomorphism can be considered as a recurrence of the old, in so far as it is based on material errors and on arbitrary interpretation of microscopic images; however, a new quality is displayed, which can be described as *hunting after aberrant forms* or as *provocation of bacterial variation*. This direction of studies is certainly not devoid of interest, although it is not much concerned with morphology proper, for evidently morphology can never be founded on the teratology of living beings, but only on their normal cycle of evolution proceeding under normal conditions.

Excluding the somewhat obscure point about reproduction forms, these recent researches on Azotobacter have added nothing essentially new to the classical notions about its morphology. Based on observations of continuity, they could not confirm Löhnis' somewhat sensational as well as quite improbable data about the four life cycles, the symplasm, and the metamorphosis into a "schlanken sporenbildenden Bacillus" and into a multitude of other bacterial forms. Nevertheless, they refrained, on the whole, from direct criticism of Löhnis' assertions.

A crucial point in Azotobacter morphology, which has puzzled all observers, old and new, ever since its discovery, has been left out of consideration by all of them, and that is, Why does this organism produce such a variety of aberrant forms?

The most probable explanation of this phenomenon is to be sought in the composition of the standard media in which this organism was grown from the beginning, and which were unsuitable for its normal development. The autochthonous soil and water organisms are very sensitive to concentrated laboratory media; it can thus be thought that the transfer from soil conditions into a 2 per cent glucide solution, not to mention proteid media, can easily change them from the norm. In fact, a more suitable mode of culture greatly reduces the production of aberrant forms. But this question will be discussed elsewhere.

The writer would like to emphasize again that the morphology of every organism, bacteria included, can be based only on its normal evolution cycle. To disentangle the biotype from its variants and to discover the conditions under which it is able to display a regular course of evolution, is to be regarded as the first task of the morphologist. If he is successful, he will obtain a biologically correct conception of the organism's morphology as well as the proof that the external conditions are in conformity with its adaptations.

The conditions that lead to rich cultures are commonly regarded as best for a given species and standardized for its culture. The writer, however, has tried elsewhere to attract attention to the fact that abundant growth is not always normal growth. For it is not to be forgotten that dystrophy can lead not only to atrophy but also to hypertrophy, by which the production of living substance, though abundant, is nevertheless distinctly pathological. A curious example of this kind, which can be termed hypertrophical degeneration, is reported by Roelofsen (17). While comparing strains of Thiorhodaceae grown in peptone media and in inorganic media, he noticed that growth in the former was "much more abundant" and "the yield of bacteria markedly higher" than in the latter. A microscopic examination of the "peptone bacteria" showed, however, "big and quaint forms" and much reduced motility. "Hence it must be concluded," he adds, "that these bacteria were abnormal in a morphological as well as in a physiological sense" (p. 54).

These considerations have perhaps a limited importance for medical and industrial bacteriology. But the agrobiologist, whose task it is to study the activity of genuine soil agents, should evidently take care not to modify the soil organisms, either morphologically or physiologically. The long list of standard media used plays then a rather unfortunate part in agrobiology. Our notions about the activities of soil microörganisms would certainly gain in clearness if only few media were used, but these should be carefully tested and found to be well chosen for the needs of the species. To this end a tentative method was proposed by the writer, which seems to have attracted but little attention (25).

In view of all these considerations, the writer does not quite understand the reasons why this new pleomorphism has been favorably accepted, even welcomed, as it appears, by some American bacteriologists.

Herbert C. Ward (19) thinks "that many of our earlier ideas in regard to the morphology of the bacterial cells must be subjected to rigid scrutiny, and the new conceptions recently advanced will, if proved, modify our entire point of view with respect to these microscopical organisms."

Paul Clark (4) believes that "Everyone who has examined ordinary stained preparations 'of such and such bacteria' grown on a variety of media will have noted the occurrence of aberrant morphological types to such a degree that the fixed morphology concept must be discarded."

Arthur T. Henrici, in his interesting monograph (7, p. 1), in stating his opinion about the problem of morphological variation of bacteria, thinks it "a healthy sign that within recent years, through the activities of a small but persistent group of modern pleomorphists, bacteriology is definitely breaking away from the Cohn-Koch tradition and is seriously reopening for discussion and investigation the old problem of morphologic variation in bacteria." After mildly criticizing the papers of these modern pleomorphists (Almquist, Hort, Löhnis, Mellon, and Enderlein), he nevertheless concludes, that "throughout these papers one is impressed with the meagerness and the haphazard character of the observations as compared with the widespread importance of the conclusion." "Most of the cell types described as extraordinary reproductive bodies," he has encountered "only in the death phase; it seems therefore more likely that they are cells which are undergoing retrogressive changes than cells which embark upon some new mode of growth" (p. 147). Finally, he states that the proof of complex life cycles in bacteria has never been brought forward. As can be seen, there is a far reaching concordance between the criticisms of this author and that of the writer concerning the evidence brought forward by the modern pleomorphists. Only it seems that Henrici's general opinion about the new pleomorphism, which is decidedly sympathetic, is not supported by both of these criticisms.

A last question arises, as to why the early botanical work on the morphology of bacteria, which the writer has tried to recapitulate in the present paper, has been so completely forgotten by modern morphologists. It may be, that the explanation of this disregard can be found in the opinion sometimes encountered, that bacteriology practically begins with R. Koch and the gelatin method, all work prior or extraneous to that being in a sense prehistoric or negligible. The writer hopes that he has demonstrated that this way of thinking has singularly narrowed the viewpoint on the morphological problem and on the doctrine of pleomorphism, which can most certainly be much better understood if more closely examined in an historical light.

The writer further believes that the standard pure culture method, so indispensable when the mass effect of a microbial agent is to be studied, is far from being infallible where morphological studies are concerned. As was

seen by the example of Azotobacter, the operator, misled by the belief in the perfection of his method and influenced by his theories, does not hesitate to include all sorts of impurities in one and the same life cycle. In any case, a test of purity is often difficult to devise and is not generally required from the operator, his assertion being considered sufficient. So erroneous ways remain open to every observer who has not acquired a wider morphological training.

In comparing the bacteriological pure culture method with the old botanical method, where stress was laid on continuous observation of selected cells or groups in microculture, the latter presents decided advantages for the study of *normal evolution*, by following step by step the development of the strain and by comparison of its stages with the growth found in the natural habitat. With sensitive soil and water organisms, this method better than any other can prevent the observer from being misled by aberrant forms.

In connection with these considerations, the recent researches on sulfur bacteria would appear particularly instructive to morphologists. The writer refers to the very remarkable researches of van Niel (18), who succeeded in obtaining irreproachably pure cultures of these organisms and in elucidating their physiology. But when he tried to study the morphology of his pure strains, he found the results "most discouraging . . . The longer the pure culture was kept under careful observation the more it became obvious that any satisfactory identification with genera and species created before was impossible" (pp. 66, 67). In fact, every strain of Chromatium or Thiocystis presented in pure culture something like a mixture of all genera and species established by the writer, Bavendamm, and others. It is then hinted, that this obsolete taxonomy should be abandoned since it stands in disagreement with the results of the pure culture method.

The writer would rather reproach the pure culture method for leading to results that are not in conformity with the natural evolution of these bacteria.

The arguments upholding this opinion seem irrefutable:

All observers noted unanimously the regular, round and oval shapes of Chromatium and Thiocystis strains in their natural habitat.

The growth of every strain was continuously followed by the writer during weeks and months and was observed to go regularly through its own short cycle, and that in strictly identical conditions, often under the same coverglass; the influence of different external factors being thus excluded.

The description of van Niel, and even more his figures, tell us that after the pure culture operations nothing is left of these regular forms, the growth being composed nearly exclusively of strikingly diverse, distorted, blown, quaint shapes, whose nature as aberrant, or abnormal, forms can scarcely be doubted.

The only possible explanation of this change is that the strains have been thrown out of their norm, their treatment having in some unknown way

deeply affected their formative functions. The seemingly thriving state of the cultures is not an objection against abnormality, as has been explained.

The case is analogous to that of Azotobacter, but more pronounced in the sense that with the former the regular course is still clearly distinguishable among the aberrant forms, whereas with the latter the aberrant forms seem to crowd out the normal ones entirely.

On the whole, it may well be that the writer's old taxonomy of Thiobacteria—the fruit of studies of relatively short duration—has its imperfections and ought to be revised. Nevertheless, the writer is convinced, that the direct method of observation applied 50 years ago is likely to give a more adequate idea of the *normal morphology* of the sulfur bacteria than is within the scope of the most nearly perfect of pure culture methods.

REFERENCES

(1) Bachinskaya, A. A. 1935 On the structure and development of Azotobacter. *Bul. State Inst. Agr. Microbiol.* [Russian] 6: 1–47.

(2) Bary, A. de 1885 Vorlesungen über Bakterien. Leipzig.

(3) Billroth, Th. 1874 Untersuchungen über die Vegetationsformen der *Coccobacteria septica*. Berlin.

(4) Clark, Paul F. 1928 Morphological changes during the growth of bacteria. *The Newer Knowledge of Bacteriology and Immunology*, p. 38–45. Edited by E. O. Jordan and I. S. Falk, Univ. Chicago Press, Chicago, Ill.

(5) Cohn, F. 1872 Beiträge zur Biologie der Pflanzen, vol. 1. Kern, Breslau.

(6) Cohn, F. 1875 Beiträge zur Biologie der Pflanzen, vol. 1, part 3. Kern, Breslau.

(7) Henrici, Arthur T. 1928 Morphologic Variation and the Rate of Growth of Bacteria. C. S. Thomas, Springfield, Ill., p. 1–194.

(8) Krassilnikov, N. A. 1931 The evolution of Azotobacter in connection with the problem of pleomorphism. [Russian] *Jour. Microbiol.* 12: 16–30.

(9) Löhnis, F. 1921 Studies upon the life cycles of the bacteria. *Mem. Nat. Acad. Sci.* 16, Second memoir: 1–335.

(10) Löhnis, F., and Hanzawa, J. 1914 Die Stellung von Azotobacter im System. *Centbl. Bakt.* (II) 42: 1–8.

(11) Löhnis, F., and Smith, N. R. 1916 Life cycles of the bacteria. *Jour. Agr. Res.* 6: 675–702.

(12) Nägeli, C. 1877 Die niederen Pilze. R. Oldenbourg Munchen, p. 1–285.

(13) Niemeyer, L. 1924 Azotobacter Studien. *Bot. Arch.* 7: 363.

(14) Petschenko, B. 1930 Über die Biologie, die Morphologie und den Entwicklungszyklus von Mikroorganismen der Azotobactergruppe. *Centbl. Bakt.* (II) 80: 161–162.

(15) Ray-Lankester, E. 1873, 1876 *Quart. Jour. Micr. Sci.* On a peach-coloured bacterium—Bacterium rubescens. 13 (new series): 408–425 (1873); Further observations on a peach- or red-coloured bacterium—Bacterium rubescens. 16 (new series): 27–40 (1876).

(16) Regel, S. de 1932 Entwicklungsgang von Azotobacter chroococcum. *Centbl. Bakt.* (II) 86: 44–68.

(17) Roelofsen, P. A. 1935 On Photosynthesis of the *Thiorhodaceae*. Diss. Rotterdam, p. 1–127.

(18) van Niel, C. B. 1931 On the morphology and physiology of the purple and green sulphur bacteria. *Arch. Mikrobiol.* 3: 1–112.

(19) WARD, HERBERT C. 1928 The newer knowledge of the morphology of bacteria. *The Newer Knowledge of Bacteriology and Immunology*, p. 1–13. Edited by E. O. Jordan and I. S. Falk. Univ. Chicago Press, Chicago, Ill.

(20) WARMING, E. 1876 Om nogle ved Danmarks Kyster levende Bakterier. Videnkabelige Meddelelser Kopenhagen. 1875, no. 20–28, p. 3–116. French abstract 1876, p. 1–36.

(21) WILCKE, F. 1930 Über die Formenfälle in Kulturen bei Azotobacter chroococcum. *Bot. Arch.* 30: 307–343.

(22) WINOGRADSKY, S. 1887 Über Schwefelbakterien. *Bot. Ztg.*, 45: 489–507, 513–523, 529–539, 545–559, 569–576, 585–594, 606–610.

(23) WINOGRADSKY, S. 1888 Beiträge zur Morphologie und Physiologie der Bacterien. I. Zur Morphologie und Physiologie der Schwefelbacterien. Arthur Felix, Leipzig, p. 1–120.

(24) WINOGRADSKY, S. 1926 Études sur la microbiologie dur sol. *Ann. Inst. Pasteur* 40: 455–520.

(25) WINOGRADSKY, S. 1932 Études sur la microbiologie du sol. *Ann. Inst. Pasteur* 48: 89–134.

(26) ZOPF, W. 1882 Zur Morphologie der Spaltpflanzen. Leipzig.

(27) ZOPF, W. 1883 Die Spaltpilze. Edward Tremendt, Breslau.

FORMAMIDE AND AMMONIUM FORMATE AS NITROGEN SOURCES FOR PLANTS[1]

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INTRODUCTION

The ammoniation of superphosphate and fertilizer mixtures is recognized as an excellent practice, because such treatment makes for quicker curing and good mechanical condition, neutralizes acidity, adds nitrogen, reduces bag rotting and storage difficulties and, of prime importance to fertilizer consumers, particularly those who use distributing machines and apply large rates per acre, insures good drillability and uniform distribution. Ammoniation was first successfully accomplished by treatment with either anhydrous or aqua ammonia. The reactions ensuing and the results of studies to determine the composition and availability of ammoniated superphosphate have been given consideration by different investigators (1, 2, 3, 4, 5, 6).[3] Later, a solution of crude urea in aqua ammonia, designated "Urea-Ammonia Liquor," was proposed as an ammoniation agent, and afterwards "Urea-Ammonia Liquor B" was developed as an improvement.[4] The latter is reported to consist essentially of urea, ammonia, and water in the proportions best suited for the ammoniation of superphosphate. Recently certain ammoniation solutions, designated "Crude Nitrogen Solution" and "Nitrogen Solution II," respectively, were produced[5] and offered to the trade. The former is stated to be a mixture of nitrate of soda (45%), anhydrous ammonia (45%), and water (10%). The nominal composition of Nitrogen Solution II

[1] A greenhouse study conducted in coöperation with F. W. Parker of E. I. DuPont de Nemours and Co., Wilmington, Delaware, for the purpose of evaluating formamide and ammonium formate as nitrogen sources for plants. Dr. Parker made arrangements with other agricultural agencies, including the Alabama, Rhode Island, and West Virginia Agricultural Experiment Stations, to conduct similar studies and report independently. In this connection interesting reports by C. J. Rehling, Alabama Station, and J. C. Taylor, West Virginia Station, have been submitted. The different nitrogen compounds used in the greenhouse study were furnished by Dr. Parker, who also kindly offered suggestions concerning experimental procedure.

[2] Senior and Assistant Biochemist, respectively, Division of Soil Fertility Investigations.

[3] References given represent only a partial list of available publications on the ammoniation of superphosphate.

[4] Urea-ammonia liquors were produced, and the process patented, by E. I. DuPont de Nemours and Co., Inc. (U. S. Patent No. 1,894,136, Jan. 10, 1933.)

[5] Produced by The Barrett Company.

is by weight stated to be: ammonium nitrate (60%), neutralizing ammonia (20%), water (20%). Both the urea-ammonia liquor and the nitrogen solutions are considered to be serviceable in the preparation of either complete fertilizers or base mixtures.

More recently, formamide ($HCONH_2$) containing about 30 to 31 per cent of nitrogen has been proposed as a substitute for water in the preparation of urea-ammonia liquor, to increase the nitrogen content of the ammoniating solution. Formamide is of interest as a potential nitrogenous fertilizer material because of its possible use in ammonia liquors that are commonly used in the treatment of superphosphate and in the preparation of mixed fertilizers containing superphosphate. Formamide is a liquid that is miscible with ammonia and water in all proportions and is also an excellent solvent for nitrogenous compounds commonly used in ammoniating liquors. Its use would, therefore, make possible the production of a wide range of ammoniating liquors of high concentration, containing a high proportion of fixed, chemically combined ammonia. When the formamide liquor is added to superphosphate the formamide hydrolyzes to ammonium formate,

$$HCONH_2 + \xrightarrow{H_2O} HCOONH_4,$$

possessing a high degree of stability and insuring very little, if any, reversion of available phosphorus. Ammonium formate, when pure, contains between 22 and 23 per cent of nitrogen.

OBJECT OF PRESENT STUDY

Although there is little probability that formamide would ever be used directly as a source of nitrogen in fertilizers, nevertheless its proposed use in ammoniating solutions makes it essential to determine its value and that of its hydrolytic product, ammonium formate, as nitrogen sources for plants. If either, particularly the latter, should prove to be undesirable as a source of nitrogen, obviously the inclusion of formamide in ammoniating liquors is ruled out. The greenhouse studies presented here had as an objective the evaluation of formamide and ammonium formate as nitrogenous fertilizer materials from the standpoint of their efficiency in promoting the growth of plants in comparison with two standard nitrogen sources, ammonium sulfate and urea.

GREENHOUSE POT CULTURE STUDIES

The greenhouse studies, comparing formamide and ammonium formate with ammonium sulfate and urea, were conducted in 1 gallon glazed pots holding 5 kgm. of soil. The soil types used were (*a*) Caribou loam, pH 5.4; (*b*) Norfolk loamy fine sand, two samples, pH 5.3 and 6.6, respectively. Ordinary superphosphate furnished phosphoric acid at the rate of 240 pounds of P_2O_5 per acre; muriate of potash supplied K_2O at the rate of 120 pounds per acre; and the different nitrogen sources furnished 80 pounds of nitrogen per acre, making

these applications equivalent to a ton of 4–12–6, the acre-rate of application employed in these experiments.[6] Each nitrogen source was used in the preparation of 4–12–6 mixtures with an 0–12–6 mixture serving as a control. To all mixtures magnesium sulfate was added at the rate of 30 pounds of MgO per ton of fertilizer and, in addition, each mixture was rendered neutral by the addition of finely ground dolomitic limestone. The different mixtures were incorporated with the soil by means of a mechanical mixer. Oats, wheat, and millet were grown as indicator crops in the different series of tests, the plant growths obtained being reported in the accompanying tables on an oven-

TABLE 1

*Results with oats comparing formamide and ammonium formate with urea and ammonium sulfate as nitrogen sources in complete fertilizer**

NITROGEN† SOURCE IN 4–12–6 MIXTURE	ACTUAL AND RELATIVE WEIGHTS OF OATS, 20 PLANTS, GROWN ON DIFFERENT SOIL TYPES:						AVERAGE YIELDS ALL SOILS	
	Caribou loam (pH 5.4)		Norfolk loamy fine sand (pH 5.3)		Norfolk loamy fine sand (pH 6.6)			
	Actual	Relative	Actual	Relative	Actual	Relative	Actual	Relative
	gm.		*gm.*		*gm.*		*gm.*	
Urea	9.8	114	11.8	358	12.3	300	11.3	213
Ammonium sulfate	10.3	120	11.0	333	11.7	285	11.0	207
Formamide	11.2	131	12.3	373	12.0	293	11.8	222
Ammonium formate	11.5	135	12.7	385	13.2	322	12.5	234
½ Formamide, ½ ammonium formate	9.5	111	11.7	354	11.9	290	11.0	207
½ Urea, ½ formamide	10.6	124	11.8	357	12.0	293	11.5	217
½ Urea, ½ ammonium formate	11.1	130	12.6	382	11.5	280	11.7	220
⅓ Urea, ⅓ ammonium sulfate, ⅓ formamide	10.9	128	11.2	339	11.4	278	11.2	211
⅓ Urea, ⅓ ammonium sulfate, ⅓ ammonium formate	10.2	119	11.0	333	11.1	271	10.8	203
P-K (0–12–6)	8.5	100	3.3	100	4.1	100	5.3	100

* Planted September 17, 1935; harvested November 14, 1935.

† Nitrogen basis. Fertilizer applied at rate of 2000 pounds per acre.

dry weight basis. After oats were sown, the roots were screened out, the soil was refertilized as originally, and wheat planted. After the wheat was harvested, the roots were screened out, and millet was planted (Tables 1, 2, 3).

DISCUSSION OF RESULTS

Oats. As far as the results with oats are concerned, given in table 1, it is evident that both formamide and ammonium formate proved to be good

[6] The different 4–12–6 mixtures used in the pot tests were prepared under the supervision of Dr. W. H. Ross, Division of Fertilizer Research, Bureau of Chemistry and Soils, who was interested in making studies relative to the influence of formamide and ammonium formate on physical properties of the mixtures in which they were incorporated.

TABLE 2

*Results with wheat comparing formamide and ammonium formate with urea and ammonium sulfate as nitrogen sources in complete fertilizer**

NITROGEN SOURCE IN 4–12–6 MIXTURE	ACTUAL AND RELATIVE WEIGHTS OF WHEAT, 20 PLANTS, GROWN ON DIFFERENT SOIL TYPES						AVERAGE YIELDS ALL SOILS	
	Caribou loam (pH 5.4)		Norfolk loamy fine sand (pH 5.3)		Norfolk loamy fine sand (pH 6.6)			
	Actual	Relative	Actual	Relative	Actual	Relative	Actual	Relative
	gm.		*gm.*		*gm.*		*gm.*	
Urea	9.7	188	10.4	298	9.6	240	9.9	235
Ammonium sulfate	10.7	208	11.5	328	12.6	316	11.6	276
Formamide	9.1	178	9.8	280	8.9	214	9.3	221
Ammonium formate	8.7	170	9.1	260	8.9	212	8.9	212
½ Formamide, ½ ammonium formate	10.2	199	10.4	297	10.5	264	10.4	248
½ Urea, ½ formamide	9.0	176	9.6	274	10.4	260	9.7	231
½ Urea, ½ ammonium formate	7.5	146	10.1	288	10.2	256	9.3	221
⅓ Urea, ⅓ ammonium sulfate, ⅓ formamide	10.0	195	10.9	313	11.2	321	10.7	254
⅓ Urea, ⅓ ammonium sulfate, ⅓ ammonium formate	9.1	177	10.0	287	9.7	242	9.6	219
P-K (0–12–6)	5.1	100	3.5	100	4.0	100	4.2	100

* Planted December 3, 1935; harvested February 5, 1936.

TABLE 3

*Results with Hungarian millet comparing formamide and ammonium formate with urea and ammonium sulfate as nitrogen sources in complete fertilizer**

NITROGEN SOURCE IN 4–12–6 MIXTURE	ACTUAL AND RELATIVE WEIGHTS OF MILLET, 20 PLANTS, GROWN ON DIFFERENT SOIL TYPES						AVERAGE YIELDS ALL SOILS	
	Caribou loam (pH 5.4)		Norfolk loamy fine sand (pH 5.3)		Norfolk loamy fine sand (pH 6.6)			
	Actual	Relative	Actual	Relative	Actual	Relative	Actual	Relative
	gm.		*gm.*		*gm.*		*gm.*	
Urea	14.1	180	15.2	276	18.3	326	15.9	252
Ammonium sulfate	17.8	228	18.8	342	20.2	360	18.9	300
Formamide	20.4	261	17.0	309	19.4	346	18.9	300
Ammonium formate	17.1	219	17.8	323	20.5	366	18.5	293
½ Formamide, ½ ammonium formate	19.3	254	21.1	383	20.4	364	20.3	322
½ Urea, ½ formamide	17.0	218	20.8	378	19.7	351	19.2	304
½ Urea, ½ ammonium formate	16.4	210	17.5	318	21.0	375	18.3	290
⅓ Urea, ⅓ ammonium sulfate, ⅓ formamide	18.7	240	22.2	403	23.8	425	21.6	342
⅓ Urea, ⅓ ammonium sulfate, ⅓ ammonium formate	19.6	251	15.0	272	18.4	328	17.7	281
P-K (0–12–6)	7.8	100	5.5	100	5.6	100	6.3	100

* Planted February 20, 1936; harvested April 15, 1936.

nitrogen sources; in fact, proved somewhat better than either urea or ammonium sulfate. The effect of soil reaction in the case of the Norfolk soils was not significant. The soil with pH 6.6, however, gave a greater weight of oat plants for the control set (0–12–6 treatment) than the soil having a pH of 5.3.

Wheat. The results with wheat, table 2, are the reverse of those with oats, in that neither formamide nor ammonium formate produced as high yields as did either urea or ammonium sulfate. It is to be noted, however, that the combination of formamide and ammonium formate proved superior to urea alone. Again soil reaction exerted very little influence on growth.

Millet. With millet as the indicator crop, results were obtained, table 3, indicating clearly a favorable response to formamide and ammonium formate

TABLE 4

Results with Hungarian and German millet comparing formamide and ammonium formate with urea and ammonium sulfate as nitrogen sources in complete fertilizer

Soil type: Norfolk loamy fine sand (pH 5.8)

SERIES I—HUNGARIAN MILLET			SERIES II—GERMAN MILLET		
Source of nitrogen	Dry weight of plants (30)		Source of nitrogen	Dry weight of plants (30)	
	Actual	Relative		Actual	Relative
	gm.			*gm.*	
Urea	76.2	425.7	Urea	44.5	176.5
Ammonium sulfate	79.7	445.3	Ammonium sulfate	40.3	160.0
Formamide	71.5	399.4	Formamide	39.9	158.3
Ammonium formate	78.6	439.1	Ammonium formate	37.6	149.2
½ Urea, ½ ammonium sulfate	74.0	413.4	½ Urea, ½ ammonium sulfate	42.9	170.0
P-K (0–12–6)	17.9	100.0	P-K (0–12–6)	25.2	100.0

as nitrogen sources. In this test with millet, the Norfolk soil with the higher pH (6.6) usually gave higher yields than the soil with a pH of 5.3. In table 4, results are given for Hungarian and German millet. In the case of the Hungarian millet, ammonium formate proved superior to urea and was practically on a par with ammonium sulfate; while formamide fell below any of the other nitrogen sources. With German millet both formamide and ammonium formate gave yields below the standard nitrogen sources. After the Hungarian millet was grown, April 14 to June 10, 1936, the roots were screened out, the soil was refertilized, and planted to German millet, July 7 to September 9.

SUMMARY

Formamide has been proposed as a constituent in ammonia liquors used in the ammoniation of superphosphate. When superphosphate is treated with

formamide-urea-ammonia liquor, the formamide is converted by hydrolysis to ammonium formate which is reported as stable in the mixture.

Greenhouse pot studies were made to evaluate formamide and ammonium formate as nitrogen sources in complete fertilizer for oats, wheat, and millet. A total of eleven tests were made comparing these nitrogen sources with urea and ammonium sulfate. Considering all tests, formamide was better than urea five times and ammonium formate was better than urea seven times. Compared with ammonium sulfate both formamide and ammonium formate produced higher yields four times. Expressed as total dry weight yield for all indicator crops on the different soils, the formamide mixture produced 231.5 gm.; the urea mixture, 231.9 gm.; the ammonium formate, 235.7 gm.; the ammonium sulfate, 244.6 gm.; and the control, P-K mixture, 101 gm.

It is probably true that the nitrogen in formamide and ammonium formate under normal soil conditions is converted fairly quickly to nitrate form. This fact helps to explain the response of oats, wheat, and millet to these compounds. The results of the vegetative pot tests show that formamide and ammonium formate compared favorably with the standard nitrogen sources.

REFERENCES

(1) JACOB, K. D. 1930 Composition of ammoniated superphosphate. *The Phosphorus Digest.* Nov. 1930: 5–6.

(2) JACOB, K. D., AND ROSS, W. H. 1931 Chemical nature and solubility of ammoniated superphosphate and other phosphates. *Jour. Amer. Soc. Agron.* 23: 771–787.

(3) KEENEN, FRANK G. 1930 Reactions occurring during the ammoniation of superphosphate. *Indus. and Engin. Chem.* 22: 1378–1382.

(4) KEENEN, FRANK G. 1932 Available phosphoric acid content of ammoniated superphosphate. *Indus. and Engin. Chem.* 24: 44–49.

(5) ROSS, WM. H., JACOB, K. D., AND BEESON, K. C. 1932 Report on phosphoric acid—Composition and fertilizer efficiency of the insoluble phosphates in ammoniated superphosphates. *Jour. Assoc. Off. Agr. Chem.* 15: 227–266.

(6) WHITE, L. M., HARDESTY, J. O., AND ROSS, WM. H. 1935 Ammoniation of double superphosphate. *Indus. and Engin. Chem.* 27: 562–567.

PLATE 1

FORMAMIDE AND AMMONIUM FORMATE AS NITROGEN SOURCES IN COMPLETE FERTILIZER FOR OATS

FIG. 1. On Caribou loam.

FIG. 2. On Norfolk loamy fine sand No. 13—P-K; No. 1—Urea; No. 2—Ammonium Sulfate; No. 3—Formamide; No. 4—Ammonium formate; No. 5—½ Formamide; ½ Ammonium Formate; No. 6—½ Urea, ½ Formamide; No. 7—½ Urea, ½ Ammonium Formate.

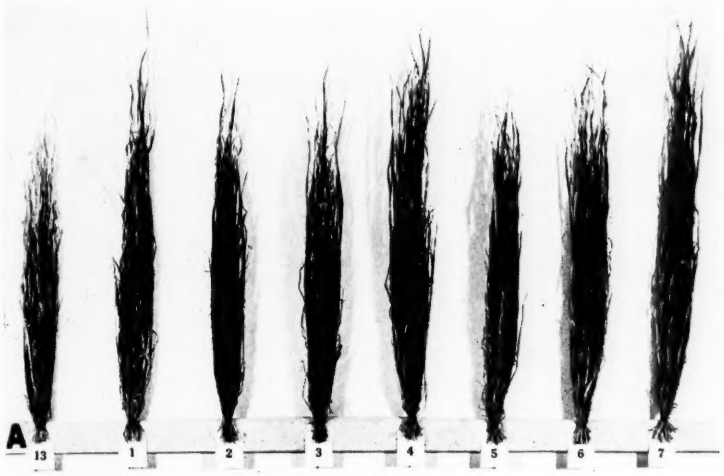

FIG. 1

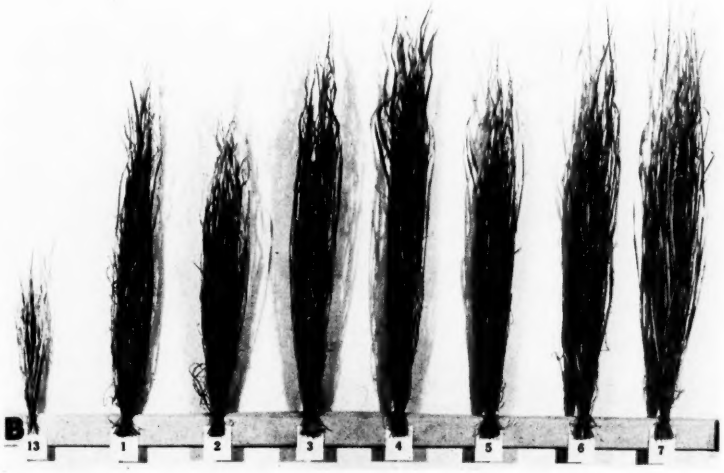

FIG. 2

COMPOSITION OF THE LEAF LITTER OF FOREST TREES

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The relatively undecomposed organic débris which characterizes the uppermost layer of a forest soil profile is composed, for the most part, of mature dead leaves from trees. Through the process of decomposition, the nutritional constituents of the litter are returned to the soil where they enter the soil solution, the exchange complex, and the drainage waters. Forest soils differ from those used for ordinary agricultural crops in that they are seldom cultivated or fertilized artificially. The maintenance of good forest soil fertility is, to a large degree, contingent on the periodic return of plant nutrients to the surface of the soil in litter, their subsequent release, and their incorporation after decomposition.

The factors which affect the rapidity and course of decomposition of litter can be placed in two broad categories: chemical and physical properties of the litter material, and environmental factors, climate, and soil (4).

It has been shown many times, in the laboratory, that the rate and course of decomposition of forest organic débris is determined by differences in its chemical composition, if the microflora are the same, and the exterior conditions are optimal.

The following chemical constituents and properties of litter are important in determining the rate and nature of decomposition (7):

(*A*) Calcium content—largely because of its influence upon reaction and the microbial population
(*B*) Buffer characteristics
(*C*) Nitrogen—both as proteins and amino acids
(*D*) Celluloses and hemicelluloses
(*E*) Lignin
(*F*) Fats, oils, and waxes
(*G*) Tannins
(*H*) Silica

This report is concerned with the amounts of four constituents, nitrogen, carbon, ash, and calcium, in the mature undecomposed leaf litter of nine species of trees in the Duke Forest. The nine species are: loblolly pine (*Pinus taeda* L.), shortleaf pine (*P. echinata* Mill.), red cedar (*Juniperus virginiana* L.),

[1] The writer is indebted to Mr. Robert Dick, Research Assistant, for making many of the analytical determinations.

white oak (*Quercus alba* L.), black oak (*Q. velutina* La Marck), red gum (*Liquidambar styraciflua* L.), yellow poplar (*Liriodendron tulipifera* L.), red maple (*Acer rubrum* L.), and dogwood (*Cornus florida* L.). Eight of the litter samples were taken from trees growing in Georgeville silt loam; the yellow poplar was on Congaree silt loam. All of the soils of the Piedmont Plateau in the locality adjacent to the Duke Forest are low in calcium, and these two soils are especially low.

The litter samples were collected at maturity in the autumn of 1934 from recently fallen leaves, with the exception of red cedar litter, which was composed of both mature and green leaves. McHargue and Roy (3) found that nitrogen content decreases with the age of leaves. Calcium content is known to increase with the age of leaves.

Nitrogen was determined by a modification of the Gunning method; carbon, by the Parr method; ash, by prolonged ignition in a muffle furnace; and

TABLE 1

Total nitrogen content and carbon-nitrogen ratio of forest litter

SPECIES OF LITTER	NUMBER OF DETERMINATIONS	MEAN PERCENTAGE OF NITROGEN	STANDARD DEVIATION	STANDARD ERROR OF MEAN	C/N RATIO
White oak	11	1.246	0.004	0.001	39.9
Red cedar	11	1.132	0.007	0.002	44.9
Black oak	11	1.104	0.009	0.003	45.9
Dogwood	11	0.999	0.004	0.002	48.4
Shortleaf pine	29	0.982	0.014	0.002	52.9
Loblolly pine	11	0.891	0.003	0.001	58.6
Yellow poplar	25	0.811	0.020	0.004	61.6
Red gum	12	0.626	0.003	0.001	80.0
Red maple	12	0.497	0.009	0.003	97.9

calcium, by precipitation as the oxalate from a hydrochloric acid extract of the ash.

ANALYSIS OF DATA

Sufficient determinations of each constituent were made for each composite sample of litter to evaluate statistically the significance of the differences between means of any two species. If the difference between means exceeded three times the standard deviation of the difference, then it was considered real.

The nine species are listed in the order of decreasing nitrogen content in table 1. The table also includes the statistical measures used to characterize data obtained in simple sampling, in addition to the mean. The differences between mean nitrogen content are all statistically significant.

The standard deviation measures the extent to which the individual observations are scattered about the mean. On the average, 68 per cent of the observations lie within the standard deviation on either side of the mean. In

the analysis of these data, individual observations were discarded if their deviation from the mean exceeded 2.5 times the standard deviation. The probability of the deviation from the mean of a single observation exceeding 2.5 times the standard deviation is only about 3 in 100 in the case of 11 observations.

For 11 observations, the chances are only 1 in 67 that the true mean lies outside 3 times the standard error; and with 29 observations, the chances are only 1 in 370 that the true mean lies outside 3 times the standard error on either side of the mean.

The standard error is useful in determining the number of observations necessary to obtain a desired accuracy. In the case of nitrogen in yellow poplar, it was calculated that 18 determinations would be necessary to obtain

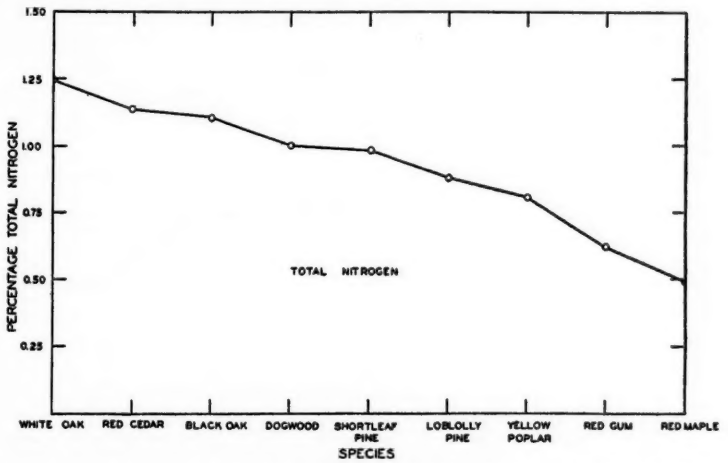

FIG. 1. TOTAL NITROGEN CONTENT OF MATURE, UNDECOMPOSED LITTER FROM NINE SPECIES OF FOREST TREES

a mean the maximum error of which was ±0.010 per cent, and 71 determinations to obtain a mean the maximum error of which was ±0.005 per cent.

TOTAL NITROGEN CONTENT

Litter of white oak has the highest nitrogen content, 1.25 per cent, and that of red maple the least, about 0.50 per cent (fig. 1). Melin (4) also found the nitrogen content of red maple to be low, 0.37 per cent. Litter of dogwood, black oak, red cedar, and white oak have nitrogen contents between 1.00 and 1.25 per cent, whereas litter of shortleaf pine, loblolly pine, yellow poplar, red gum, and red maple have nitrogen contents between 0.50 and 1.00 per cent. In 23 species of litter investigated by McHargue and Roy (3), the highest nitrogen content, 3.12 per cent, was found in black locust.

CARBON

The litter of both loblolly pine and shortleaf pine have a rather high carbon content, 53.0 per cent, whereas red cedar litter has about 51.0 per cent carbon, and dogwood litter has the least, slightly more than 48.0 per cent (fig. 2). Differences in carbon content are slight and not statistically significant and have little influence on the carbon-nitrogen ratio, which is determined largely by differences in nitrogen content.

CARBON-NITROGEN RATIO

Red maple and red gum litter have relatively high carbon-nitrogen ratios of 98 to 1 and 80 to 1, respectively, whereas white oak litter has the lowest

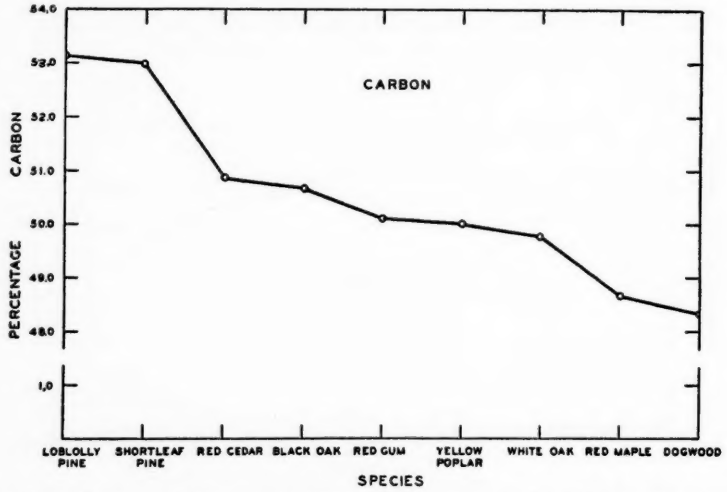

FIG. 2. TOTAL CARBON CONTENT OF MATURE, UNDECOMPOSED LITTER FROM NINE SPECIES OF FOREST TREES

ratio, 40 to 1 (fig. 3). The carbon-nitrogen ratio is often correlated negatively with rate of decomposition. On the basis of field observations, however, there appears to be little correlation in the case of the nine species involved. The high silica, tannin, and lignin contents and low calcium content of white oak litter apparently offset the advantages of its low carbon-nitrogen ratio. Loblolly pine and shortleaf pine litter also decomposes rather slowly. A high content of lignin and ether-soluble substances appears to be an important factor in the decomposition of the leaf litter of these species.

ASH

Dogwood and white oak litter contain rather large amounts of ash, more than 7.50 per cent, whereas the pines are low in ash, 3.00 to 3.50 per cent (fig. 4).

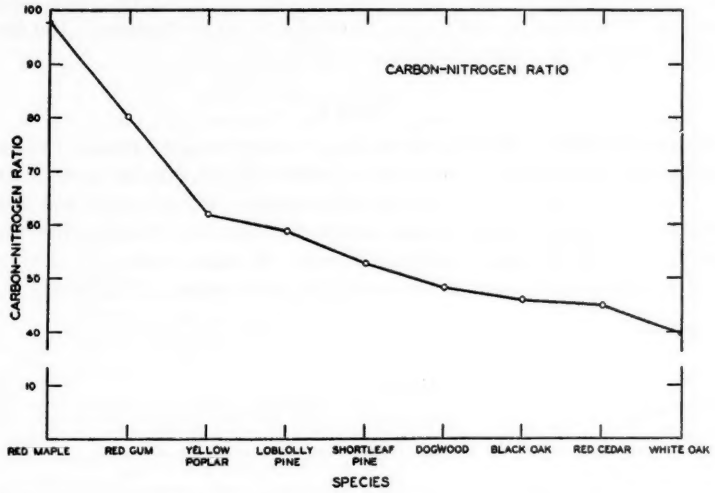

FIG. 3. CARBON-NITROGEN RATIO OF MATURE, UNDECOMPOSED LITTER FROM NINE SPECIES OF FOREST TREES

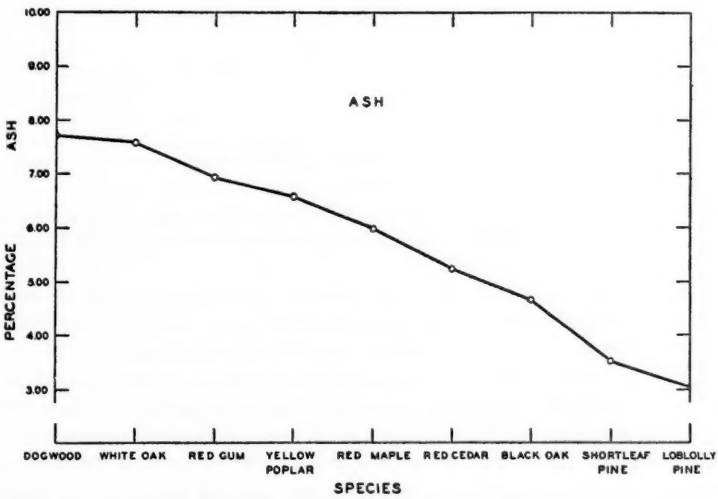

FIG. 4. TOTAL ASH CONTENT OF MATURE, UNDECOMPOSED LITTER FROM NINE SPECIES OF FOREST TREES

All differences in total ash content are statistically significant. McHargue and Roy (3) reported an ash content of 19.64 per cent for basswood litter from trees growing in the limestone section of Kentucky.

CALCIUM

Calcium content of litter on the basis of oven-dry weight separates the nine species into two categories: those with a relatively high calcium content, 2.00 to 3.50 per cent, including dogwood, yellow poplar, and red cedar; and those with a relatively low calcium content, 0.40 to 1.10 per cent, including the other species, with loblolly pine containing the least. Calcium content, on the basis of ash weight, maintains approximately the same order. All differences in

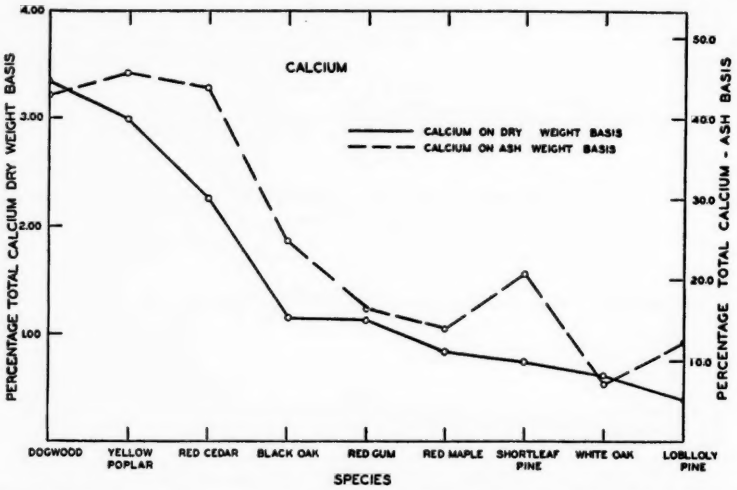

FIG. 5. TOTAL CALCIUM CONTENT ON AN OVEN-DRY WEIGHT BASIS, AND ON AN ASH WEIGHT BASIS, OF MATURE, UNDECOMPOSED LITTER FROM NINE SPECIES OF FOREST TREES

calcium content on an oven-dry weight basis are statistically significant, except the differences between red maple and shortleaf pine. All differences in calcium content on an ash weight basis are statistically significant.

A number of investigators have reported large differences in calcium content of mature leaves and other plant material. Sunflower plants have been found to be characteristically rich in calcium, whereas corn plants are poor (5). Plice (6) found that leaves of arborvitae were high in calcium, 2.6 per cent, whereas those of red maple were relatively low, with 0.8 per cent. McHargue and Roy (3) found the calcium content of dogwood litter on limestone soils to be 4.21 per cent, whereas pine oak contained only 1.36 per cent.

Garstka (2) found a positive correlation between total calcium and replaceable calcium in forest débris; an inverse relationship between replaceable

calcium and H-ion concentration; and a relationship between H-ion concentration and nitrogen transformation.

The calcium content of litter has a profound influence on the H-ion concentration of the F and H layers, as well as the A_1 horizon of forest soils. Coile (1) found the reaction of the three organic horizons to be characteristically different in seven forest types in the Duke Forest. Litter of the pines and oaks are relatively acid, with a reaction of about pH 4.1, whereas the litter of red cedar has a reaction of about pH 6.0.

The amount of certain constituents in the mature leaf litter of forest trees is apparently characteristic for any given species. A knowledge of the chemical components of various species of litter will enable foresters to approach more scientifically the problem of determining suitable mixtures of species in forest stands. Pure stands of certain species, such as loblolly pine, shortleaf pine, and white oak, probably are not conducive to the development of the best humus type in this region because of inherent characteristics of the litter which influence the rate and type of decomposition. It appears likely that certain understory species, such as dogwood, may have beneficial effects on forest soil fertility.

REFERENCES

(1) Coile, T. S. 1933 Soil reaction and forest types in the Duke Forest. *Ecology* 14: 323–333.

(2) Garstka, W. U. 1932 The calcium content of Connecticut forest litter. *Jour. Forestry* 30: 396–405.

(3) McHargue, J. S., and Roy, W. R. 1932 Mineral and nitrogen content of the leaves of some forest trees at different times in the growing season. *Bot. Gaz.* 94: 381–393.

(4) Melin, Elias 1930 Biological decomposition of some types of litter from North American forests. *Ecology* 11: 72–101.

(5) Newton, J. D. 1928 The selective absorption of inorganic elements by various crop plants. *Soil Sci.* 26: 85–91.

(6) Plice, M. J. 1934 Acidity, anti-acid buffering, and nutrient content of forest litter in relation to humus and soil. Cornell Univ. Agr. Expt. Sta. Mem. 166.

(7) Waksman, S. A. 1936 Humus. Williams and Wilkins Co., Baltimore.

THE MINERALOGICAL COMPOSITION OF THE VERY FINE SANDS OF SOME PENNSYLVANIA SOILS[1]

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INTRODUCTION

The importance of the mineralogical composition of soils has been generally recognized for many years, but detailed study has been seldom attempted, and the literature on the subject is relatively scanty. More information along this line is desirable, as has been pointed out by Milner (6), Plummer (7), McCaughey and Fry (5), and others. The presence of a great variety of minerals in the soil has been recognized for many years, but quantitative data have been lacking, which makes comparisons of different soils from a mineralogical standpoint difficult. The purpose of this investigation was to study quantitatively the mineral composition of the very fine sand separates of five Pennsylvania soils. In the course of this study, improved methods for the separation of the mineral groups were developed, and these are herein described.

HISTORICAL

The presence of a great variety of minerals in soils was noted by McCaughey and Fry (5), who in 1913 reported the results of mineralogical studies on the chief soil groups in the United States. They identified optically 34 different minerals in a great variety of soils and concluded that the mineralogical composition of soils varies with the physiographic regions in which they occur. The results, although of interest from a qualitative standpoint, are in no sense quantitative; hence, actual comparisons are difficult.

Hendrick and Newlands (4) studied some English and Scotch soils, using methods outlined by Steinreide (9). These methods include separations by means of heavy liquids and the electromagnet. Their results are expressed on a quantitative basis. They concluded that the very fine sand fraction is of

[1] A portion of a thesis submitted to the faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

The writer wishes to express his appreciation for the helpful suggestions and criticisms tendered by Dr. A. P. Honess, Department of Geology, the Pennsylvania State College, under whose general direction this work was done, and to Professor E. Truog, Department of Soils, the University of Wisconsin, for valuable suggestions in the preparation of this manuscript.

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great value in establishing the real significance of the origin of the soil. On the basis of their results, they could distinguish between English and Scotch soils chiefly because of differences in the amounts and varieties of the ferro-magnesium minerals found in the very fine sand fractions. Volk (11), in studying the formation of muscovite in soils, reports quantitative separations of mineral groups by means of liquids of different specific gravities. He made no effort to identify the various minerals, with the exception of muscovite, feldspar, and quartz, in the different fractions, as his problem was to trace the formation of secondary muscovite.

Plummer (7) studied the relationship between the fertilizer requirements of some North Carolina soils and their chemical and mineralogical composition. He concluded that mineralogical analyses were valuable as a supplement to chemical analyses, to determine how certain inorganic plant food elements occur in the soil.

DESCRIPTION OF SOILS

In view of the fact that mineralogical studies of Pennsylvania soils have received so little attention, with the exception of work by Thomas and Honess (10) on Hagerstown silt loam, five Pennsylvania soils were selected for this study. They were, according to the Bureau of Soils Classification (2), Dekalb sand, designated Dekalb A, and Dekalb clay loam, designated Dekalb B, Hagerstown silt loam, Lackawanna sandy loam, and Volusia clay loam.

These soils, according to Shaw (8) and Coffey (1), were derived as follows:

Dekalb sand and clay loam, west of the Allegheny escarpment from soft sandstones and carboniferous shales, and east of the Allegheny crest from hard sandstones and thin bedded shales

Hagerstown silt loam, the result of weathering and solution of Trenton limestone, representing the residue after the carbonates of the original rock had been dissolved away

Lackawanna sandy loam, from the slight glaciation of red sandstones and shales, made up of a mixture of material transported some distance by the glaciers

Volusia clay loam, from the same source as the Lackawanna sandy loam, except that the sandstones and shales are not red; rests on an impervious hard pan

PLAN OF STUDY

Mechanical analyses of the soils described and subsequent quantitative separation of the very fine sand separates into three general mineral groups by means of liquids of different specific gravities constituted the method of study. After the separation of these mineral groups, the various mineral species were identified by standard petrographic methods, the abundance of different minerals was estimated, and their occurrence in pounds per acre in the soils calculated. By this means, the mineralogical composition of the very fine sands of the soils could be compared.

The work reported was confined to the very fine sand separate, because preliminary examinations showed that certain mineral species are not prominent until the size of the fragments approach that of the very fine sand. This is in agreement with the work of Hendrick and Newland (4), McCaughey and Fry (5), and others. The separates finer than the very fine sand were not investigated because of the difficulty of separation and identification, although their importance is recognized. These fine separates are to be studied and reported on later.

METHODS

Mechanical Analysis

The mechanical analysis was carried out using the methods recommended by the U. S. Bureau of Soils (3), except that a 50 gm. sample was used instead of a 5 gm. sample. This modification was necessary in order to obtain a sufficient quantity of the soil separates for subsequent treatment with the heavy liquids. The results of the mechanical analyses are given in table 1.

TABLE 1

Mechanical analyses of the five soils

SOIL SEPARATES U. S. BUREAU OF SOILS, PARTICLE SIZE LIMITS	PERCENTAGES OF SEPARATES IN FIVE SOILS				
	Dekalb A sand	Dekalb B clay loam	Lackawanna sandy loam	Volusia clay loam	Hagerstown silt loam
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
Fine gravel	9.83	2.06	17.29	3.80	3.19
Coarse sand	22.15	1.39	8.11	1.85	2.42
Medium sand	33.75	4.51	6.72	2.26	2.48
Fine sand	16.37	14.65	4.83	4.06	1.79
Very fine sand	10.63	24.44	18.87	21.38	14.31
Silt	7.08	30.60	23.23	39.96	50.61
Clay	0.33	19.60	16.42	20.97	18.70
Loss on ignition	0.00	2.00	4.00	5.15	6.13
Total	100.14	99.25	99.47	99.43	99.63

The quantitative separation of the soil minerals into groups

The method of separation of minerals of different specific gravities by means of heavy liquids has been known for many years. Various heavy liquids have been used, including Thoulet's solution, methylene iodide, acetylene tetrabromide, Clerici's solution, bromoform, and S-tetrabromethane (12). In this study, bromoform was used because of the ease of recovery after use and convenience in diluting, or concentrating, to various densities. The separations were made by means of a centrifuge and a specially constructed separatory funnel, details of which will be given later. The separates were weighed and the fractions expressed in terms of percentages of the respective soil separates.

Separation into groups was made as follows:

Heavy group—minerals having a specific gravity greater than 2.86
Quartz group—minerals having a specific gravity less than 2.86 but greater than 2.62
Feldspar group—minerals having a specific gravity less than 2.62

Bromoform. The bromoform used was of U.S.P. purity and had a specific gravity of about 2.58. The specific gravity was easily raised by boiling on a hot plate for about an hour, and before use, the specific gravity was always determined by means of a pycnometer which had been carefully checked against boiled distilled water at 22°C. (approximately room temperature). If bromoform having a specific gravity of 2.62 was desired, the bromoform was diluted with petroleum ether. This solution, on standing, may change in specific gravity because of evaporation of the petroleum ether. In order to insure the correct specific gravity of this solution, there was placed in it a small crystal of orthoclase (sp. gr. 2.56) and one of quartz (sp. gr. 2.65). If the specific gravity of the solution is correct, the orthoclase should float, and the quartz sink.

Petroleum ether. The petroleum ether used for washing the residues and in diluting the bromoform was the U.S.P. grade, having a specific gravity of 0.662.

Alundum Crucibles. This type of crucible, when used in the proper kind of adapter, is excellent for filtering the various residues by means of suction. It is essential in work of this character that no rubber should be used where there is a chance of its being wet with bromoform. For this reason, all bromoform should be stored in flasks with either ground glass stoppers or corks, and in all filtering operations caution should be used wherever rubber is employed.

Separatory Funnels. Funnels with straight side walls were made especially for this work, special attention being given to the stop cocks. In making these stop cocks, the plug must be ground in place and the hole then drilled, otherwise difficulties will arise from leakage of bromoform. The funnels were fitted with a cork carrying a glass stirring rod.

Analytical Procedure. Place 5 cc. of bromoform of the proper specific gravity and 1 to 2 gm. of the oven-dried soil separate into the separatory funnel, stir well, and insert the cork. The soil is conveniently kept in a weighing bottle, and the amount used determined by difference. Place the separatory funnel into the centrifuge cup, being sure that the cups are carefully balanced to avoid vibration, and the funnel turned so that the large part of the stop cock is on the outside, otherwise, the stop cock will be forced out when the centrifuge is started and the determination ruined. Centrifuge for 5 minutes at about 1,200 r.p.m. Remove the funnel from the centrifuge, draw off the heavy minerals into a previously ignited and weighed alundum crucible, and remove adhering bromoform by suction. Replace the bromoform that has been drawn off with the heavy minerals, stir carefully, and repeat the centrifuging. After centrifuging and drawing off five times, the separation is practically complete. After all of this group has been collected in the alundum crucible, wash it about 6 times with petroleum ether, dry in an electric oven at 100°C. for 30 minutes,

cool in a desiccator, and weigh. Pour the lighter minerals left in the separatory funnel onto a dried filter paper, wash with petroleum ether, dry, and retain for the next separation.

The separation of the three general groups of minerals was accomplished in the above manner, the only difference being in the specific gravity of the bromoform solution used.

The fractions were checked by means of the microscope, and in all cases the separation was practically complete. Contamination with an occasional fragment of a lighter, or heavier, mineral was observed, due probably to

TABLE 2

Completeness of separation of heavy mineral group in very fine sand on successive treatments, using bromoform of 2.86 sp. gr.

SUCCESSIVE SEPARATIONS	A 2.4357 GM. SAMPLE		B 2.2824 GM. SAMPLE	
	gm.	*per cent*	*gm.*	*per cent*
Recovered in first separation	.0380	1.56	.0429	1.92
Recovered in second separation	.0312	2.84	.0199	2.78
Recovered in third separation	.0150	3.46	.0074	3.10
Recovered in fourth separation	.0071	3.74	.0034	3.25
Recovered in fifth separation	.0026	3.86	.0022	3.34

TABLE 3

Amounts of three specific gravity groups in very fine sand separates

SOILS FROM WHICH VERY FINE SAND SEPARATES WERE DERIVED	HEAVIER THAN SP. GR. 2.86		HEAVIER THAN SP. GR. 2.62 BUT LIGHTER THAN 2.86 MOSTLY QUARTZ		LIGHTER THAN SP. GR. 2.62 MOSTLY FELDSPAR	
	per cent	*lbs. per acre*	*per cent*	*lbs. per acre*	*per cent*	*lbs. per acre*
Lackawanna sandy loam	3.60	13,586	95.8	361,549	0.60	2,264
Hagerstown silt loam	1.29	3,692	85.2	243,842	13.51	38,666
Volusia clay loam	1.98	8,466	89.6	383,130	8.42	36,004
Dekalb sand	0.97	2,062	88.9	189,001	10.13	21,536
Dekalb clay loam	0.97	4,742	98.0	479,902	1.03	5,034

aggregation during the process of centrifuging, but this was not enough to vitiate the results.

In all separations, care must be used to see that the temperature is constant, especially in the separation of the two lighter fractions. A slight change of temperature may cause the bromoform to change in specific gravity sufficiently to prevent proper separation. The influence of this change in temperature may be overcome by observing the maximum temperature of the centrifuge for the speed used for making the separation, and then adjusting the specific gravity of the heavy liquid to this temperature.

To avoid any leakage of bromoform around the stop cock, it is necessary to use a heavy stop cock grease. A very satisfactory grease is one made of 3 parts paraffin, 2 parts vaseline, and 1 part soft rubber, melted together. It is

necessary to clean the funnels with cleaning solution and to regrease the stop cocks of the separatory funnels before each determination. Table 2 gives the results of an experiment to determine the number of times that it is necessary to centrifuge a sample in order to make a complete separation.

On the basis of the data in table 2, it was decided for the purposes of this study to repeat the heavy liquid separation five times.

The amounts of the three mineral groups in the very fine sands of the five soils were then determined by the methods just described, and the data obtained are set forth in table 3.

TABLE 4

*Occurrence of various minerals in the very fine sand separate of the soils indicated**

MINERAL	HAGERSTOWN SILT LOAM	VOLUSIA CLAY LOAM	DEKALB SAND AND CLAY LOAM	LACKAWANNA SANDY LOAM
Tourmaline	+	+	+	+
Zircon	+	+	+	+
Hornblende	+	+	+	+
Rutile	+	+	+	−
Muscovite	+	+	+	+
Chlorite	+	+	+	+
Epidote	+	+	+	−
Garnet	+	+	+	+
Cyanite	+	−	−	+
Microcline	+	+	−	−
Orthoclase	+	−	−	−
Plagioclase	+	+	−	−
Quartz	+	+	+	+
Magnetite	−	+	+	+
Iron Oxide	+	+	+	+
Corundum	−	+	−	−
Titanite	−	+	+	−
Leucoxene	−	+	−	−
Fluorite	−	−	+	−
Augite	−	−	−	+
Hematite	−	−	−	+
Sericite	−	−	−	+

* + denotes present; − denotes absent.

It will be noticed that these fractions from the different soils vary considerably as far as the percentage composition is concerned. These variations appear more striking when considered in terms of pounds per acre in the plowed layer.

After making the quantitative separation of the mineral groups, the various minerals were identified in temporary mounts by the usual petrographic procedures, and the completeness of separation of the quartz and feldspar fractions studied. Table 4 lists the different minerals identified in the very fine sand separates of the five soils studied.

Permanent mounts were then made, using Canada balsam as a mounting media, and from these, counts were made to determine the relative abundance of the various minerals. After counts had been made, the proportions by weight of the various heavy minerals were computed, using the specific gravities of the different minerals as a basis. The weights of feldspar and quartz were determined directly by weighing the amounts in each case. The results for the five soils studied are given in table 5.

DISCUSSION

The mineralogical study of the very fine sands is of considerable value, because a preliminary examination of the various separates revealed the fact that the mineralogical characteristics of soils become prominent when the size of the fragments approach that of the very fine sand. This is in agreement with Hendrick and Newlands (4), McCaughey and Fry (5), Plummer (7), and others.

TABLE 5

Proportions of various minerals in heavy group of the very fine sand separate of the soils indicated

MINERALS	PERCENTAGES BY WEIGHT IN HEAVY FRACTIONS OF SOILS INDICATED				
	Lackawanna sandy loam	Hagerstown silt loam	Volusia clay loam	Dekalb A sand	Dekalb B clay loam
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
Zircon	5.6	18.4	21.7	23.2	35.5
Tourmaline	5.8	8.9	12.2	8.4	4.8
Muscovite	16.3	10.6	15.9	18.7	2.4
Iron Oxide	50.8	49.2	31.4	49.7	53.2
Chlorite	16.0	5.8	16.6	....	1.0
Hornblende	5.6	3.8	1.1	....	1.1
Rutile	....	....	....	....	1.9

Since this study deals primarily with the quantitative determination of the different mineral species, it is well first to consider the methods of separation. The fact that good checks are obtained upon weighing the fractions is not conclusive evidence that separation has been complete; in order to be more certain, microscopic examination is necessary. Microscopic examination is also necessary to bring out the importance of making such separations.

A careful inspection of the heavy groups of minerals of the soils studied reveals the fact that the minerals present are similar, differing only in proportion and quantity. This is brought out in tables 3 and 4. It is true that very small quantities of other heavy minerals occur in some soils, for example, corundum in Volusia clay loam, fluorite in Dekalb sand and clay loam, and cyanite in Hagerstown silt loam and Lackawanna sandy loam, etc., but these unusual minerals occur only in very small amounts and may or may not be characteristic of the soil. Examining table 5 further, one finds that the outstanding minerals are zircon, tourmaline, muscovite, iron oxide, chlorite,

hornblende, and rutile. Any comparisons or correlations attempted should, therefore, be based upon these groups of minerals.

Table 6 gives the actual weights of minerals present in the very fine sand separates of the soils studied, expressed in pounds per acre. As far as the heavy residues are concerned, only those minerals which were relatively abundant are included.

The proportion of the various minerals present in the heavy fractions is given in table 5. This might give an erroneous impression of the actual quantities of minerals one would expect in these soils. Considering, however, the total amounts given in table 6, the actual condition existing in the soils becomes clear. It is apparent that the total quantities of heavy minerals present in the very fine sands of these soils vary greatly. It may be possible by further study to establish certain heavy mineral limits for different soils, which would assist in soil classification.

TABLE 6

Amounts of minerals present per acre plowed layer in very fine sand of five soils

MINERALS	LBS. PER ACRE OF MINERALS IN VERY FINE SAND SEPARATES				
	Lackawanna sandy loam	Hagerstown silt loam	Volusia clay loam	Dekalb A sand	Dekalb B clay loam
	lbs.	*lbs.*	*lbs.*	*lbs.*	*lbs.*
Zircon	761	679	1,837	478	1,683
Tourmaline	788	329	1,033	173	228
Muscovite	2,215	391	1,346	386	114
Iron Oxide	6,902	1,816	2,685	1,025	2,523
Chlorite	2,174	214	1,405	.....	47
Hornblende	761	140	93	.....	52
Rutile	.....	.....	.....	.....	90
Feldspars	2,264	38,666	36,004	21,536	5,034
Quartz	361,549	243,842	383,130	189,001	479,902

The quartz fractions were similar, with the exception of that from the Hagerstown silt loam. This soil appears to contain considerable amounts of authigenic quartz. This appears to be typical of Hagerstown soil, since this type of quartz was not noted in any of the others.

The feldspars in the soil have always been of interest to the soil worker because they are the source of a large part of the potash. In Dekalb sand and clay loam and Lackawanna sandy loam, potash feldspars are notably lacking. The feldspars noted in these soils proved to be plagioclase, which contain little potash. In the Hagerstown silt loam and Volusia clay loam, large quantities of feldspars were observed, which were chiefly microcline, with a trace of plagioclase (albite). This accounts in part for the large amounts of potash found in these soils on chemical analysis. This is also of interest from the standpoint of plant growth. Soils of both the Hagerstown and Volusia series lack available potash, as is shown by many field experiments. In both soils,

potash is a limiting factor in plant growth in spite of the fact that large amounts of potash-bearing minerals are present. This is not surprising, when the insolubility of microcline is taken into consideration.

SUMMARY

The mineralogical composition of the very fine sand separates of five Pennsylvania soils was studied in detail, as follows:

The very fine sand was separated by mechanical analysis and subsequently subdivided by means of heavy liquids into three mineral groups, namely:

(a) The heavy mineral group, consisting of minerals having a specific gravity greater than 2.86

(b) The quartz group, minerals having a specific gravity greater than 2.62 but less than 2.86

(c) The feldspar group, minerals having a specific gravity less than 2.62

In the course of the study, improved methods were developed which were used to separate the mineral groups quantitatively according to their specific gravities.

After separation of the mineral groups, the various minerals were identified by standard petrographic methods, and the relative proportions estimated. The results obtained made it possible to compare the mineralogical characteristics of the very fine sand separates of the soils studied.

It was concluded that:

The mineralogical composition of the very fine sand separates varied considerably as to amounts, but not as to variety, of mineral species.

In the mineralogical study of soils, certain generally occurring minerals are useful for purposes of comparison and correlation. In the case of the Pennsylvania soils studied, these minerals are feldspars, zircon, tourmaline, muscovite, chlorite, hornblende, and rutile.

It was possible to study quantitatively the occurrence of certain minerals in the soil and to use data thus obtained as an aid in soil classification.

REFERENCES

(1) Coffee, G. N. 1912 A study of the soils of the United States. *U. S. Dept. Agr., Bur. Soils Bul.* 85: 48–65.

(2) Davis, R. O. E., and Bennett, H. H. 1927 Grouping of the soils on the basis of mechanical analysis. *U. S. Dept. Agr. Dept. Cir.* 419: 8.

(3) Fletcher, C. C., and Bryan, H. 1912 Modification of the method of mechanical soil analysis. *U. S. Dept. Agr. Bur. Soils Bul.* 84.

(4) Hendrick, J., and Newlands, G. 1923 The value of mineralogical examination in determining soil types, with a method of examination and comparison of English and Scotch soils. *Jour. Agr. Sci.* 13: 1–18.

(5) McCaughey, W. J., and Fry, W. H. 1913 The microscopic determination of soil forming minerals. *U. S. Dept. Agr. Bur. Soils Bul.* 91.

(6) Milner, H. B. 1929 Sedimentary Petrography, ed. 2, 470–471.

(7) PLUMMER, J. K. 1914 Relation of the mineralogical and chemical composition of the fertilizer requirements of North Carolina soils. *N. C. Tech. Bul.* 9.
(8) SHAW, G. W. 1914 The soils of Pennsylvania. *Penn. State Col. Bul.* 132: 221–228.
(9) STEINREIDE, F. 1921 Anleitung zur mineralogischen Bodenanalyse. 2 Aufl. Leipzig. W. Englemann.
(10) THOMAS, W., AND HONESS, A. P. 1923 Complete analysis of Hagerstown silt loam. *Soil Sci.* 15: 1–17.
(11) VOLK, N. J. 1933 Formation of muscovite in soils, and refinements in specific gravity separations. *Amer. Jour. Sci.* 26: 114–129.
(12) WINCHELL, A. N. 1928 Principles of Optical Mineralogy, ed. 3., pt. I: 29–30.

OCCURRENCE OF MASSES OF GELATINOUS MICROBES IN THE SOIL

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In some mountainous regions in the central part of Japan, the inhabitants have known for a long time that there are localities where a quantity of gelatinous substance is found underground. The general belief that this substance is good to eat made it of interest to them; hence the popular appellation *Tengu-no-mugimesi* is given to this queer substance. (Tengu is a sort of demi-god popular in Japanese folklore. *Tengu-no-mugimesi* means boiled barley of Tengu.)

The inhabitants' knowledge of this substance seems to date as far back as a century, and we can find articles about it in some guide books, or local geographies, of that day. Since the dawn of modern science in Japan, this curious matter naturally has attracted the notice of investigators, and a number of reports have already been published. These include Ôno (5), Kawamura (3), Molisch (4), Kato, et al. (2), and Takahashi (6). The majority of these papers were, however, published in Japanese, or in local journals which are seldom read by soil science investigators, so that it may be useful to give here a brief account of this substance.

DISTRIBUTION

About 17 localities where the substance occurs can be enumerated from those studied by the writer, or reported in former publications. It does not seem to be very widely distributed. All of the localities hitherto known are concentrated in, or very near, the border line of the northern region of the province of Sinano, which is situated in the central part of Japan. They are in two groups, the river Sinano running between them. The group east of the river is distributed from 138° 22′ to 138° 30′ east longitude, and from 36° 15′ to 36° 30′ north latitude. About 11 localities belong to this group, and almost all of them are found in the vicinity of Mt. Asama, an active volcano. The group west of the river (about 6 localities) is distributed from 138° 5′ to 138° 15′ east longitude, and from 36° 40′ to 36° 50′ north latitude. Mt. Kurohime and Mt. Iduma, important volcanoes, are in the latter region.

The gelatinous mass in question is found distributed on, or near, these volcanoes. It is noteworthy that similar substance has not been reported, so far, from any other part of Japan.

ALTITUDE AND INCLINATION

The localities so far reported without exception lie not lower than 700 m. above sea level; 10 localities are found between about 1,500 and 2,000 m., and the remaining 7 between 700 and 800 m. Therefore, they can be divided into two groups from the viewpoint of vertical distribution.

The inclinations of these localities are not uniform. Some are found on a horizontal plane, but the majority are in somewhat inclined grounds. In some extreme cases, the slopes are as steep as 40° (fig. 1).

MANNER OF OCCURRENCE OF THE GELATINOUS MASSES

In these localities, we find layers of a gelatinous mass in the soil. Naturally, the occupied areas are not uniform in size. Besides, the gradual transition in the peripheral part from the gelatinous mass to the soil makes it extremely difficult to delineate the border line, so that exact measurement of the area is impracticable. As far as one can judge with the unaided eye, however, the occupied area extends in some cases for more than 300 sq. m. Exact measurement of the thickness of the layer of gelatinous material is also impossible for the same reason as above. But even that part of the layer that is composed of only the gelatinous mass is more than 50 cm. thick in some cases. Usually, the layer seems to be 10–20 cm. thick. At any rate, the total mass of this substance in the soil in each locality must be quite remarkable.

The general appearance of the substance is not uniform. We can distinguish, for example, (*a*) a slimy, rather translucent, irregular mass (fig. 3), often appearing as a thin film covering the surface of rocks in the soil; (*b*) an opaque, granular form (fig. 4); and (*c*) an opaque, clayey mass (fig. 5). There are, of course, intermediate forms also.

Of these three types, (*a*) is colorless, or yellowish, or brownish red; and (*b*) and (*c*) are usually gray, brown, or black. It is interesting that (*a*) is especially rich in water (water content c. 95 per cent) as compared with the others, the water content of which lies between 70 and 80 per cent.

Type (*b*) is found most abundantly in a pure state. Among the enumerated localities, those of the lower altitude (700–800 m.) usually produce samples of type (*c*) and of a lower grade of purity, that is, containing a larger percentage of soil. Examination under a microscope, however, reveals that these samples may rationally be grouped with either types (*a*) or (*b*), for their essential components seem to be the same gelatinous microbes.

VEGETATION ON THE SOIL SURFACE

In some cases, the gelatinous masses are exposed directly on the soil surface, which seems, in the opinion of the present writer, to be a secondary phenomenon. Normally, the mass is covered with a soil layer 10–30 cm. thick. The surface is usually covered with a vegetation of grasses, sedges, and other dwarf herbs. The surface soil contains a large percentage of organic matter

(loss of ignition in some cases being 56 per cent on the basis of dry weight) and is always acidic in reaction (pH 4.25–6.4). Few cases are reported in which the soil surfaces are free from vegetation Such localities appear to be a sort of small desert of rock-débris. If the gelatinous mass underground is explored, we can always discern some remains of vegetable roots, which fact suggests that there possibly was plant covering on the soil surface in former days, which was destroyed from some cause or other.

NATURE OF THE GELATINOUS MASS

If we examine the gelatinous mass under a microscope, we can easily recognize that it is composed mainly of a sort or sorts of microbes encapsulated or embedded in slimy matter (fig. 6). The cells of these microbes vary from globule to long rod, straight or crooked, often with swollen ends. In short, they are quite irregular in appearance, often giving the impression of being involution forms. As for their size, the width is usually 0.5–1.0μ, and when they assume the form of long rods, their length measures up to about 7μ. Two to four granules of a strong refractivity are often recognized in the body. The cell bodies are enclosed in capsules, or in slime, as stated above. The capsules are usually globular, or oval, in outline, and sometimes we can discern the concentric structure. The number of cells in one common capsule is not constant, a large one containing as much as 40 cells. The slimy mass assumes, naturally, no definite shape.

Samples of the translucent type are mainly composed of slimy microbes mixed with some capsulate forms, whereas those of other types are composed, for the most part, of the capsulate forms. From the qualitative point of view, however, we cannot establish a definite distinction among them, so that it seems convenient to treat them provisionally under one general category.

The problem of whether these microbes of different shapes are variations in the life history of one and the same species, or varieties of several species, or represent distinct species, cannot be easily determined.

As for their staining properties, a detailed report is given by Kawamura (3), according to whom most of the bacterial stains are applicable. They are especially well stained with Lugol's solution, which property can be conveniently utilized in the case of microscopic examination.

The position of these microbes in systematic botany is also problematic. Ôno (5) and Kawamura (3) are of the opinion that they are capsulate bacteria, and the latter author coined a new scientific name, *Vulcanothrix silicophila*. On the other hand, Yendo (7) early suggested, without giving any clear reason, that they belong to Nostocaceae. Stockmeyer, who examined the sample sent by Molisch (4), recognized Cyanophyceae, belonging to the genera of Gloeocapsa, Gloeothece, Microcystis, and Lyngbya, as the characteristic components of the gelatinous mass. His identification must, however, have been done only morphologically. To those who are familiar with the peculiarities of the habitat of these gelatinous microbes, an identification based simply on

morphological characters is not to be accepted without reservations. Further investigations in detail, especially of their physiological characters, are much wanted.

Besides these capsulate microbes, which are regarded as the primary elements of the gelatinous mass, there are usually observed some microbes of the actinomycetous character, about 0.5μ wide and rarely branching. Furthermore, the cultural study (plating and dilution methods usually employed to count the number of microbes in the soil) revealed the presence of ordinary peptone-decomposing bacteria, some filamentous fungi, denitrifying bacteria, Clostridia, and some unicellular algae, and proved the absence of Azotobacter cells, nitrifying bacteria, and cellulose-decomposing bacteria, both aerobic and anaerobic.

CHEMICAL PROPERTIES

Kawamura (3) noticed that the gelatinous mass contains a considerable quantity of silica and iron. According to the determination of his collaborator, the total ash, silica, and iron content of the substance in question is 13.59, 8.873, and 1.230 per cent, respectively, on the basis of the oven-dry weight; that is, about 65 per cent of the ash consists of silica,[1] and about 10 per cent of iron. This is a remarkable fact, of which a re-determination is desirable.

Later, Kakekawa (1) attempted an analysis of the substance and reported that it produces reducing sugar (presumably glucose) as the result of hydrolysis with HCl. He determined also the content of the ether-soluble portion and various forms of nitrogenous compounds. The results of his chemical analysis, combined with those of his experiments with animals on the nutritive value, led him to conclude that the gelatinous substance is of no value as human food, contrary to local tradition.

The serious difficulty in the study of the microbes in question is that we have not yet found how to grow them in artificial cultures. It is observed that the collected samples do not change in appearance over a long period in the laboratory, if they are kept sufficiently moist. This is true over a period of one year, as far as the present writer's experiment is concerned. Probably, the period can be even longer. During this period, they do not show any sign of multiplication, nor are symptoms of decomposition usually observed. They remain as fresh as when newly sampled.

If they are kept uncovered, and the free evaporation of moisture is not controlled, they lose their water and finally change into black, hard grains, or blocks, of irregular outline. On remoistening, however, these dried-up samples absorb water again by imbibition and regain their former consistency. The change is reversible, except for coloration, as the black shade is more dense

[1] The organism, named by Kawamura *Vulcanothrix silicophila*, is cited in *Soil Microbiology* by Selman A. Waksman. 2nd edition, 1932, p. 568, as an example of a high content in silica.

after the desiccation. Under the microscope as well, the remoistened material assumes almost the same appearance as the fresh one. Usual staining reactions are not effective in demonstrating the distinction. Methods to distinguish living cells from dead have yet to be investigated.

So much for the occurrence and the properties of this queer substance. There are many problems yet to be solved. The author is studying the subject under a subsidy of the Tôsyôgu Tricentenary Foundation, and plans to report further in the future. This paper constitutes an introductory and historical sketch.

SUMMARY

In the soil of some regions in the central part of Japan, there occur gelatinous masses, which are almost exclusively composed of microbes with a gelatinous capsule. The position of these microbes in systematic botany is not yet definitely settled. The present paper is a preliminary report on the description of the localities, the method of occurrence, and the microscopic and chemical properties.

REFERENCES

(1) KAKEKAWA, S. 1934 *Tengu-no-Mugimesi*, chemical compositions and animal experiments [Japanese]. Rpt. Imp. Govt. Inst. for Nutrition, 7: 122–129.

(2) KATO, M., ET AL. 1934 Studies on *Tengu-no-Mugimesi* [Japanese]. Rpt. Imp. Govt. Inst. for Nutrition, 7: 88–129.

(3) KAWAMURA, T. 1916 Studies on *Tengu-no-Mugimesi*, a massy bacterial vegetation [Japanese]. *Bot. Mag.* [Tokyo] 30: 109–119, 133–151.

(4) MOLISCH, H. 1926 Pflanzenbiologie in Japan. Jena.

(5) ÔNO, N. 1916 Untersuchungen über *Tengu-no-Mugimesi* [Japanese]. *Bot. Mag.* [Tokyo] 30: 59–65.

(6) TAKAHASHI, M. 1935 Studies on *Tengu-no-Mugimesi*. *Botany and Zoology* 3: 761–768, 925–931, 1128–1134.

(7) YENDO, K. 1911 Kaisan-syokubutugaku (Marine Botany) [Japanese]. Tokyo.

PLATE 1

FIG. 1. The summit of Mt. Asama, an active volcano. (× indicates the locality where the gelatinous mass occurs.)

FIG. 2. The gelatinous mass in situ. The figures on the tape measure indicate the depth from the soil surface.

FIG. 3. The gelatinous substance, type (*a*).

FIG. 4. The gelatinous substance, type (*b*).

FIG. 5. The gelatinous substance, type (*c*).

FIG. 6. Characteristic microbes of the gelatinous mass.

Fig.1

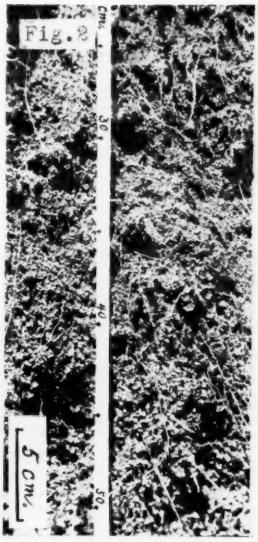
Fig.2
5 cm.

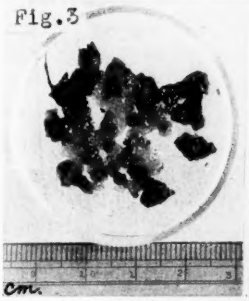
Fig.3
cm.

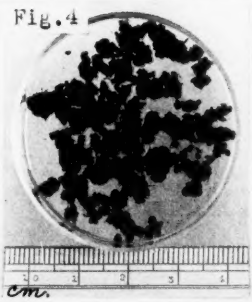
Fig.4
cm.

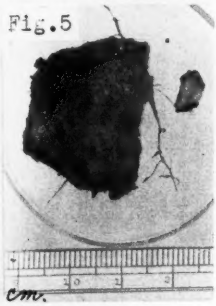
Fig.5
cm.

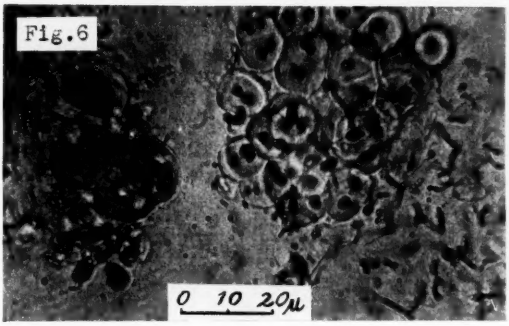
Fig.6
0 10 20μ

THE USE OF COLLAPSIBLE TUBES FOR STORING SOIL SAMPLES FOR MOISTURE ESTIMATION

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In a recent investigation of the movement of moisture in soils, it was necessary to estimate moisture content of a large number of soil samples taken in the field.

Despite the field methods of determining moisture content of soils, drying in the oven at 100–110° C. still remains the most reliable and rapid method of moisture estimation. Transportation of the samples from the field to the laboratory for this purpose requires the use of air-tight containers; otherwise some sort of waxing has to be resorted to. We have found that collapsible tubes of the type generally used for storing dental creams are excellent for this purpose. The screw cap is cut off, and the opening hammered and soldered. Of course, special tubes without the screw cap could be manufactured, but this was not considered worth while the first time. The tubes used were 10.5 cm. long and 2.5 cm. in diameter. They held 30–40 gm. of soil. The tubes are numbered in serial order with a punch mark, and the weight of each is recorded. The approximate weight of each tube is 17–18 gm., and 100 tubes can be easily carried in several cardboard boxes.

The soil sample is thoroughly mixed by hand, and about three-quarters of the tube filled with it. The mouth of the tube is closed with a pair of flat-nosed pliers by pressing the edge, and bending it over twice. The tube with the soil is brought in the laboratory and weighed. The mouth is then opened and the tube placed in a stand and dried in the oven at 100–110°C. for 24 hours and weighed again. The soil is then tipped out and the tube, after cleaning, can be used again. To test the utility of the tube under extreme conditions a number of experients were performed with the following results:

(1) Three closed tubes containing a wet soil (about 18 per cent moisture) did not lose any moisture in five days when placed in a desiccator over calcium chloride.

(2) Two closed tubes containing a wet soil did not lose any moisture in one month when kept on a shelf in the laboratory.

(3) Twenty tubes used five times for storing samples, drying, etc., did not show any appreciable change in their original weights.

(4) Nine tubes used five times for regular moisture estimation, and then heated intermittently in an electric oven for five days, did not lose any appreciable weight.

(5) Five hundred moisture determinations were made during five days, involving the use of 200 tubes; there was not a single tube breakage.

During the course of our work we tried aluminum boxes, waxed cigarette tins, tin foil wrappings, but none proved as satisfactory as the collapsible tubes. These tubes are now carried regularly by survey parties for transporting soil samples when a knowledge of moisture distribution in a freshly exposed profile is required.

It is believed that bigger tubes of the same type would be useful for carrying larger soil samples. A tube of twice the size used in these experiments could easily hold 100 gm. of soil, a quantity which would be sufficient for a complete analysis.

The tubes used by us had the following approximate composition; lead, 94 per cent; tin, 4 per cent; and aluminum, 2 per cent. We have used the same set of tubes for as many as 10 times; after this a fresh tube is desirable, though not essential.

SUMMARY

Collapsible tubes have been found extremely useful for storage of soil samples for moisture estimation. They are cheap, easy to carry, and able to withstand the rough handling to which such samples are often subjected.

A HANDY BORER FOR SOIL SURVEYORS

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Many different soil samplers have been described in this journal. These samplers and borers were of the type used for procuring samples for determinations in which the preservation of the original structure of the soil sample is necessary, e.g., for determining the pore space, the volume-weight, etc. of soils. There are also in soil science and soil investigation, especially when made for practical purposes in agriculture, instances in which the original structure can be disturbed without interfering with the purpose of the investigation.

It is especially in soil mapping that a handy soil sampler is indispensable. Using only the spade delays the work considerably, because during the mapping it is often necessary to ascertain whether the character of the soil has undergone changes. In such cases, a very small sample is sufficient for an investigation with the eye. The preservation of the original structure is not needed. The same is the case when a farmer wants to know the quality of the surface and subsurface layers of his fields.

Also, for the measurement of the variations of the reaction of a field, very small samples are sufficient. But for this purpose, investigation of the reaction of subsoil is very often necessary. Here a soil borer is required which can penetrate the soil layers quickly and without using more than a man's power.

In the soil mappings carried out during the last years by the Soil Division of the Central Agricultural Experiment Station of Finland, a certain soil borer has been used which has worked excellently in all respects. It seems advisable to describe it here, the more so because none of the samplers, borers, or augers proposed in the literature, or mentioned in the catalogues, of the different manufacturers of scientific instruments for agricultural purposes seems to meet the requirements specified above. The detailed drawing (fig. 1) shows the sampler, which consists essentially of three parts: the handle, the shaft, and the slot. The handle is of wood with a steel support, and the shaft of 12 mm. thick steel rod. The point is long and sharp, as is shown in the drawing. The borer, therefore, can be pressed carefully and without the use of a mallet in the stiffest soil.

The most important part of the borer is, however, the slot, the cross section of which is seen in the sketch. It differs from the slots of similar borers by the fact that one edge is drawn out a little and sharpened. When the borer is pressed into the earth, it must be turned to the right. Thus the slot remains

empty. The desired depth reached, the borer is turned with a rapid movement to the left, thus filling the slot with soil.

If the soil is a little moist, the sampler goes into the earth very easily without turning, and the sample obtained is free from soil particles from other horizons of the section. But even the dryest soil can be bored, if the point is long and

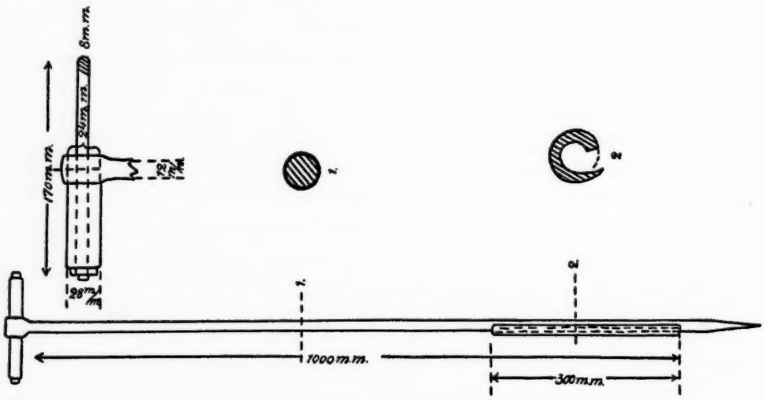

FIG. 1

sharp, and then, likewise, the sample is clean as long as the soil has the necessary cohesion.

The borer seems to be not easily manufactured as factory work, but many of the skillful Finnish village blacksmiths have made suitable units as handwork.[1]

Each of our soil surveyors uses this borer daily during the summer investigations, and the results in soil mappings have been much better.

[1] The borer is manufactured in England by Messrs. Baird & Tatlock (London) Ltd.

A NEW JACK FOR PULLING SOIL-SAMPLING TUBES

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Investigators in agronomy, soils, horticulture, forestry, and ecology often have occasion to sample for subsoil moisture. In deep soils which are fairly free from rocks and gravel, the tools most commonly used consist of a set of steel or brass soil-sampling tubes of several lengths, usually 4 and 8 feet, which are driven into the soil by means of a special "plunger" hammer, to obtain cores from various depths.

In many soils, especially when they are very wet or very dry, considerable difficulty is encountered in withdrawing the tube. Some users set a large tripod of metal or wood over the soil tube and withdraw it with a block and tackle attached to the top of the tripod. This device works well enough but is bulky and inconvenient to move about.

In 1935, Dr. F. A. Hayes, Professor of Soil Science at the University of Nebraska, while employed with the writer on investigations for the United States Forest Service, devised a lighter and more compact tool for pulling the moisture tubes. The device was used extensively in samplings made to determine the degree of depletion of subsoil moisture caused by older tree plantations and shelterbelts in the subhumid Great Plains area.

The tool consists of a hollow steel puller or wedge block (plate 1, fig. 2) which slips over the top of the soil tube; two curved steel wedges which fit snugly inside the wedge block and outside the tube; and a steel handle which is used on a wood block fulcrum to pry the tube from the soil. A downward push on the handle tightens the wedges in the block and lifts the tube from 6 to 8 inches. The process is repeated until the tube is loose enough to be withdrawn by hand. It is advisable to use a wooden, lead, or brass hammer for either separating the wedge-block from the wedges, or tightening the latter, to avoid "burring" their edges and destroying their smooth grip.

The wedge block and wedges are made of cold rolled steel, "standard" stock, carried by most machine shops. It is unnecessary to case-harden them as cold rolled steel has sufficient strength and would be more apt to break if case-hardened and subjected to any hammering while loosening the wedges. Relative hardness of wedges and soil tube affects gripping qualities, but if the jack shows any tendency to slip on the tube, a sheet of fine emery cloth placed around the tube and under the wedges (grit side in) will prevent slipping.

The size of the block may be reduced to the minimum by cutting the

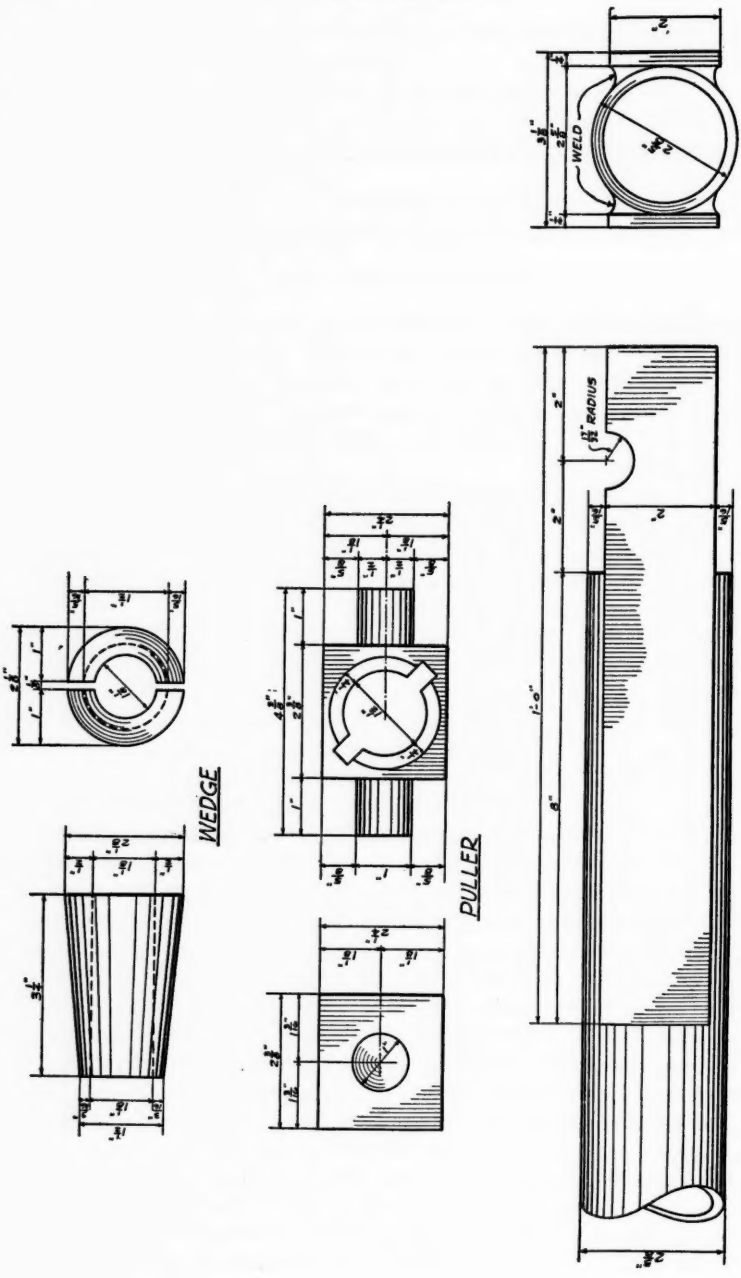

FIG. 1. Details of jack for pulling soil-sampling tubes

rectangular slots near the corners. These notches provide for the passage of the block over usual lugs on the "head" of the soil tube. The same purpose can, of course, be accomplished by using a larger block of steel with a larger cylindrical hole.

The handle consists of two notched steel plates welded at one end to opposite sides of a steel pipe 2 $\frac{5}{8}$ inches in diameter and 24 inches long (fig. 1). The notches engage the 1-inch lugs on the sides of the wedge block. Another pipe or wooden handle about 2 inches in diameter and 3 feet long is inserted in the 2$\frac{5}{8}$-inch pipe to give additional leverage.

The time for pulling the tube could no doubt be reduced by using a special fulcrum made of six 4 x 4-inch blocks of varying length, bolted together to make a series of steps 4 inches high and 4 inches wide, thus giving a fulcrum range of from 4 to 24 inches in height. The long bottom block should extend several inches beyond the others, in both directions, to increase the bearing surface and to prevent the set from tipping sideways when the highest "step" is being used as a fulcrum. Such a fulcrum would save some of the time necessary to loosen the wedges after each short lift, which must be done if a single fulcrum is available.

The complete jack costs about $12 to $15. Several have been made by the Ress Machine and Supply Company of Lincoln, Nebraska.

FIG. 1. Details of jack for pulling soil-sampling tubes

PLATE 1

FIG. 1. Jack for pulling soil-sampling tube in position and ready for action. Driving hammer is in foreground.

FIG. 2. Puller, or wedge block, and two wedges.

FIG. 3. Assembly of wedge block and two wedges in position on soil-sampling tube.

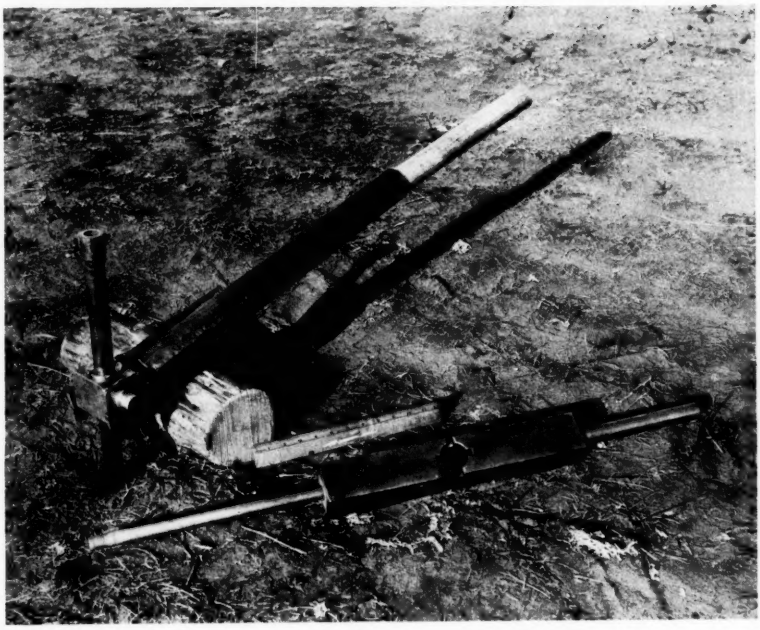

FIG. 1

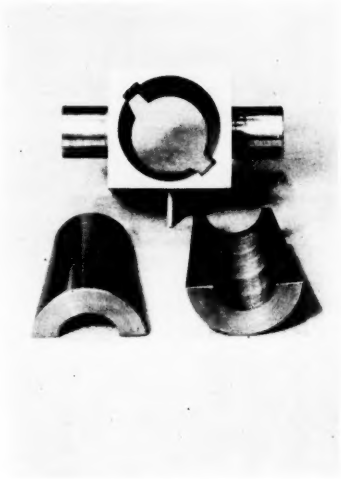

FIG. 2

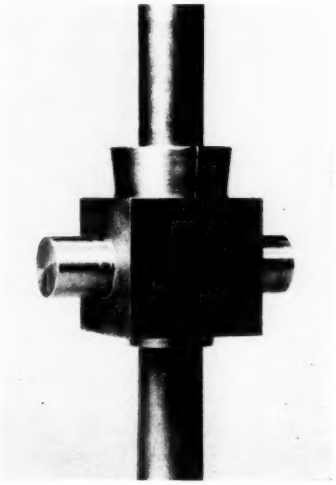

FIG. 3

THE DILATOMETER METHOD FOR DETERMINING THE MOISTURE EQUIVALENT OF SOILS[1]

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The centrifuge method (3, 4, 5) and the suction method (1) for determining the moisture equivalent of soils are empirical and depend for their accuracy upon the following of a definite arbitrary procedure. This is especially true of the centrifuge method, of which it has been shown (4, 5) that variations in the amount of soil used, thickness of the soil layer, original moisture content, oven-drying, puddling, degree of pulverization, temperature, etc., cause significant differences in the results.

Since the moisture equivalent is one of the best indexes of the physical characteristics of a soil, because it reveals in a single-value factor the texture, structure, colloidal and organic matter content, activation or nature of surface, etc., of that soil, it is essential that this highly indicative value be determined accurately and reliably by methods that are not so empirical and arbitrary as those now available.

A method which is not influenced so much by external factors and is, consequently, less arbitrary, and which tends to reduce the moisture equivalent determination to a more nearly absolute basis, is the dilatometer method. It is the purpose of this paper to present this new method. It must be stated at the outset, however, that the moisture equivalent value which the dilatometer determines is not the same in degree as that determined by the centrifuge method, but is a certain stage of moisture which is equivalent and accurate for all soils. Any stage of moisture in soils that is determined on an equivalent basis and is accurate for all soils may be designated as moisture equivalent.

PROCEDURE AND EXPERIMENTAL RESULTS

The dilatometer results were obtained according to the procedure already described (2) for determining the wilting point of soils. This original procedure was found on further experience to be satisfactory. There are certain steps in the procedure, however, that need to be emphasized for greater and more consistent accuracy. These are: (*a*) Soils that wet with difficulty should be given plenty of time to soak thoroughly, (*b*) the soils should be left at a temperature of $-10°$C. for at least 30 minutes, (*c*) the soils should be freed of

[1] Authorized by the Director for publication as Journal Article No. 285 (n. s.) of the Michigan Agricultural Experiment Station.

air, and (*d*) the operator should be careful not to be deceived by premature solidifications.

From fundamental considerations, it would be expected that the centrifuge method for determining the moisture equivalent would be influenced by external factors whereas the dilatometer method would not, at least not to any great extent. In the centrifuge method, the soil is centrifuged for the purpose of throwing out its excess water. Now it is evident that any physical factors which will impede the passage, or facilitate the retention, of water, such as impermeability due to stickiness, thickness of layer, quantity of soil, aggregation of colloids, drying in oven, temperature, etc., will influence the moisture equivalent.

TABLE 1

Influence of the quantity of soil used on the percentage of water that failed to freeze in the dilatometer

SOIL TYPE AND HORIZON	WATER THAT FAILED TO FREEZE WHEN 10 GM. OF SOIL WERE USED	WATER THAT FAILED TO FREEZE WHEN 30 GM. OF SOIL WERE USED
	per cent	*per cent*
Davidson Clay Loam B	15.7	15.4
McKenzie Clay A	23.61	23.85
Houston Clay A	20.90	20.85
Catalpa Clay B	16.75	16.3
Oktibbeha Clay B	28.4	28.73
Brookston Clay Loam A	17.15	17.43
Hagerstown Silt Clay Loam A	16.26	16.18
Marengo Clay B	34.72	35.19
Nacogdoches Fine Sandy Loam B	30.43	30.17
Buchner Silt Loam Surface	15.41	15.48
Janesville Silt Loam Surface	7.0	6.8
Marion Silt Loam Surface	9.44	8.92
Chippewa Sandy Loam A	2.52	2.50

On the other hand, in the dilatometer method the soil is supercooled to -1.0°C., then frozen at -10°C., and then brought back to -1.0°C., and that portion of the water which is not directly and immediately influenced by the adhesive and other forces of the soil is allowed to remelt. In other words, the dilatometer method measures that portion of the water which the powerful adhesive forces of the soil prevent from freezing, and this unfrozen water is independent of, and uninfluenced by, those factors which affect the centrifuge method. In this way the dilatometer method reduces the water retentiveness of soils to a more nearly absolute basis.

In tables 1, 2, and 3 are presented the results of studies on the amount of water that fails to freeze, as influenced by (*a*) the quantity of soil used, (*b*) puddling sticky soils, and (*c*) oven-drying wet, heavy clay soils. These are the

three factors which probably have the greatest influence on the centrifuge method.

The results in tables 1, 2, and 3 support the statements already made to the effect that the amount of soil used, the puddling of sticky soils, and the oven-drying of wet colloidal soils do not influence the dilatometer method as they do the centrifuge method.

There is one factor, however, which will influence the dilatometer results if it is of sufficient strength, and that is the concentration of the soil solution.

TABLE 2

Effect of puddling on the amount of water that failed to freeze in the dilatometer

SOIL TYPE AND HORIZON	WATER THAT FAILED TO FREEZE WHEN SOIL WAS NOT PUDDLED	WATER THAT FAILED TO FREEZE WHEN SOIL WAS PUDDLED
	per cent	*per cent*
McKenzie Clay A	23.58	23.41
Houston Clay A	20.72	20.56
Catalpa Clay B	16.49	16.73
Oktibbeha Clay B	28.79	28.86
Brookston Clay Loam A	17.32	17.57
Hagerstown Silt Clay Loam A	16.37	16.21
Marengo Clay B	34.98	34.69

TABLE 3

Effect of oven-drying on the amount of water that failed to freeze in dilatometer

SOIL TYPE AND HORIZON	WATER THAT FAILED TO FREEZE WHEN WET SOILS WERE AIR-DRIED	WATER THAT FAILED TO FREEZE WHEN WET SOILS WERE OVEN-DRIED
	per cent	*per cent*
McKenzie Clay A	23.70	23.45
Houston Clay A	20.48	20.75
Catalpa Clay B	16.71	16.57
Oktibbeha Clay B	28.89	28.62
Brookston Clay Loam A	17.47	17.67
Hagerstown Silt Clay Loam A	16.50	16.28
Marengo Clay B	34.64	35.08

If the soil contains large quantities of soluble salts, as do the alkali soils, the freezing point depression of the soil will be influenced accordingly and, consequently, its moisture equivalent will also be influenced. This appears to be the external factor that affects the dilatometer to the greatest extent. An extensive investigation shows that in the proportion of 20 gm. of soil to 10 cc. of water, the freezing point depression of normal, non-alkali soils is only about -0.012°C., a value which is very small and within experimental error of the bath temperatures. Accurate results, however, may be obtained by the

dilatometer method even with alkali soils by simply leaching out the salt before making the determination.

In table 4 are shown the results obtained in a comparative study of the moisture equivalent of a number of soils types, as determined by the centrifuge and dilatometer methods.

TABLE 4

*Comparison of moisture equivalent as determined by centrifuge method and by dilatometer method**

SOIL TYPE	MOISTURE EQUIVALENT AS DETERMINED BY CENTRIFUGE METHOD	MOISTURE EQUIVALENT AS DETERMINED BY DILATOMETER METHOD	RATIO OF MOISTURE EQUIVALENT BY CENTRIFUGE METHOD TO MOISTURE EQUIVALENT BY DILATOMETER METHOD
	per cent	*per cent*	
Aiken Clay Loam	28.93	16.40	1.764
Columbia Silt Loam	18.31	8.62	2.124
Delano Sandy Loam	9.09	5.10	1.784
Farwell Silt Loam	26.50	14.39	1.840
Fresno Sandy Loam	10.50	3.27	3.212
Columbia Silt Loam	16.91	6.97	2.426
Stockton Clay adobe	21.32	9.31	2.290
Hanford Fine Sandy Loam	8.84	5.27	1.678
Columbia Sand	13.02	7.78	1.672
San Joaquin Loam	17.07	5.67	3.016
Sierra Sandy Loam	11.44	5.65	2.026
Yolo Fine Sandy Loam	18.91	9.56	1.980
Placentia Loam	10.52	5.01	2.100
Madera and Gridley Loam	25.63	11.61	2.208
Oakley Fine Sand	3.29	1.48	2.224
Brookston Clay	24.51	11.35	2.160
Wooster Silt Loam	23.36	8.24	2.835
Plainfield Fine Sand	2.40	1.79	1.341
Yolo Silt Loam	21.35	10.43	2.045
Tehama Loam	13.67	6.25	2.187
Catherine Loam	37.90	19.75	1.917
Yolo Fine Sandy Loam	16.80	9.11	1.844
Yolo Clay	29.80	15.87	1.878
Yuma Sand	4.79	3.73	1.284
Brazito Fine Sand	2.58	1.65	1.564
San Joaquin Sandy Loam	13.70	5.20	2.635
Madera Sandy Loam	14.56	5.19	2.805

* Results by the centrifuge method were determined by Dr. F. J. Veihmeyer.

From an examination of the data in table 4, it is obvious that higher values for moisture equivalent are obtained by the centrifuge method than by the dilatometer method. In this connection it should be pointed out that the moisture equivalent value obtained by the dilatometer method is also the wilting point of soils. The results show also that the ratio obtained by dividing

the value for the moisture equivalent as found by the centrifuge method by that as found by the dilatometer method is not the same for all soils, but varies, and for some soils considerably. If both methods gave accurate and comparable results for all soils, and if both were not influenced by such external factors as those mentioned above, this ratio would be constant and the same for all soils, because the same major fundamental forces causing the retention of water by the soils are operative in both methods. The data in tables 1, 2, and 3 show, however, that these external factors do not interfere in the dilatometer method, and this fact, together with the fact that the wilting point of the soil is simultaneously determined, make the dilatometer method a particularly valuable one.

CONCLUSION

The dilatometer method is a valuable one for determining the moisture equivalent of soils. It possesses the following advantages:

(*a*) It is comparatively free from the influence of external factors and is consequently less empirical, and the results are on a more nearly absolute basis.

(*b*) It makes two important determinations at the same time—the moisture equivalent and the wilting point.

(*c*) It is rapid and simple.

(*d*) The apparatus required is simple and inexpensive.

REFERENCES

(1) Bouyoucos, G. J. 1934 A comparison between the suction method and the centrifuge method for determining the moisture equivalent of soils. *Soil Sci.* 40: 165–171.

(2) Bouyoucos, G. J. 1936 The dilatometer method as an indirect means of determining the permanent wilting point of soils. *Soil Sci.* 42: 217–223.

(3) Briggs, L. J., and McLane, J. W. 1907 The moisture equivalent of soils. U. S. Dept. Agr. Bur. Soils Bul. 45.

(4) Veihmeyer, F. J., Israelsen, O. W., and Conrad, J. P. 1924 The moisture equivalent as influenced by the amount of soil used in its determination. *Calif. Agr. Expt. Sta. Tech. Paper* No. 16: 1–35.

(5) Veihmeyer, F. J., Oserkowsky, J., and Tester, K. B. 1928 Some factors affecting the moisture equivalent of soils. *Trans. First Internat. Cong. Soil Sci.*

BOOK REVIEWS

Soil Erosion and Its Control. By QUINCY C. AYRES. McGraw-Hill Book Company, Inc., New York and London, 1936. Pp. xi + 365, tables 31, figs. 235. Price $3.50.

Responding to the pull of gravity, soil material is constantly moving to lower levels. Ultimately, much of it finds its way to our sea coasts. The phenomenon of soil erosion constitutes a major economic and social factor. Agricultural land is affected by tillage and other methods of soil management in a positive as well as a negative way. Rock material underlying the surface soil disintegrates more or less slowly. This process of disintegration tends to increase the depth of the soil. Soil erosion is a negative factor in that the finer soil particles are removed by moving water, by air currents, and by the mere pull of gravitation. Hence, this negative factor tends to make the layer of soil material more shallow. When man does not interfere with nature, the positive factors of soil formation may predominate. Tillage and overgrazing are responsible for the loss of enormous quantities of soil material, for deterioration in the structure of soil material, and for the loss of plant nutrients.

The present volume takes account of the various implications of soil erosion. The author's purpose in writing the book is indicated by the statement in the preface which reads: "A reversal of attitude and action in American agriculture, whereby soil wastage is eliminated and fertility accretion equals or exceeds extraction, should be a matter of grave national concern to every citizen regardless of occupation."

The book is made up of 14 chapters, an appendix, a bibliography, and an index. The designations of the several chapters follow: Introduction; Factors Affecting Rate of Erosion; Methods of Control; Rainfall and Runoff; Terrace Design; Terrace Location—Principles and Practice; Terrace Construction Methods and Machinery; Terrace Construction Costs and Maintenance; Terrace Outlets; Control of Gullies; Temporary and Semipermanent Check Dams; Permanent or Soil-saving Dams; Special Uses of Vegetation, and Soil Conservation and Land Use.

The author has rendered a helpful service to the many thousands of people in this country and abroad who are interested in the subject of soil erosion. The book will be found useful in the classroom as well as for the general reader.

Land-Reclamation in Italy. By CESARE LONGOBARDI. Translated from Italian by OLIVIA ROSSETTI AGRESTI. P. S. King & Son, Ltd., London, 1936. Pp. xii + 243, illus. 29. Price 12s 6d.

An interesting light is cast on land reclamation in Italy, both by the frontis-

piece and the contents of the eight chapters and the appendices. The frontispiece is entitled: "Mussolini, accompanied by Serpieri, Visits Maccarese, 1st March 1930." Two short statements by Mussolini are quoted by the author, namely: "To reclaim the land, and with the land the men, and with the men the race." and "The hopes and energies of the people should turn to the earth so as to draw from this primary source of prosperity, from the self-filling reservoir, the regenerating energy which must restore the serenity and wealth of the world."

The author has attempted to create a vivid picture of population pressure on the land and the effort made to diminish the dependence of Italy on imported food. The phrase *The Battle of Wheat* has become familiar to those in Italy as well as to many thousands outside that country.

At the beginning of the first chapter, the author says:

> The world-wide depression has not made us lose heart. It is impossible to believe that mankind has reached a point when there is nothing to be done but to sit by the wayside warning the on-coming generations to turn back because there the road ends and the world goes no further. On the contrary, there are many indications that the present depression marks a final stage in the elaboration of a new civilization bringing with it a life of higher spiritual and material content.

The titles of the chapters are: Towards Higher Standards of Living; General Notions on Integral Land-reclamation; Integral Land-reclamation and the Wheat Campaign; Land-reclamation Legislation; Integral Land-reclamation; Executive Organs and Procedure; Execution and Financing of Land-reclamation Works; Some Land-reclamation Described; and Mussolini on Land-reclamation. There are two appendices, whose titles follow: "Mussolini Act, 24th December 1928, VII, No. 3134; Measures for Integral Land-reclamation," and "R. Decree of 15th February 1933, XI, No. 215, containing the New Rules for Integral Land-reclamation."

The work contains many interesting illustrations, which should help the reader to visualize the recent progress of land reclamation in Italy. It is a valuable contribution to the economic and social history of the Italian people.

English Farming Past and Present. By LORD ERNLE. Edited by A. D. HALL. Longmans, Green and Co., London, 1936. Pp. xvi + 559. Price $5.00.

The reviewer recalls with pleasure his reading of the first edition of *English Farming Past and Present*, which appeared in 1912. With many of the other readers of this scholarly work, he was impressed by the mastery of the author in delineating the structure of rural life in England, its early days, and its periods of prosperity and adversity. The author was able to draw conclusions whose significance was not limited to England alone, nor even to the British Empire alone.

The present volume is a revision of Lord Ernle's work. Sir A. Daniel Hall, a well known authority on British farming, has not only made available the original material as prepared by the author but has contributed information

based on his own wide experience. Rowland E. Prothero—better known as Lord Ernle—noted in the preface to the first edition that "*English Farming Past and Present* is based on an article which appeared in the *Quarterly Review* for 1885. The article was subsequently expanded into a book, published in 1888 by Messrs. Longman under the title of *The Pioneers and Progress of English Farming*. This book has been out of print for twenty years."

In the preface to the fifth edition, Sir Daniel says:

> When Lord Ernle and Messrs. Longmans' did me the honour of asking me to prepare a new edition of 'English Farming, Past and Present' I agreed with some trepidation. I knew that I had neither the desire nor the knowledge to alter what Lord Ernle had written of 'the past.' But what in 1912 he wrote of 'the present' has since taken on a different colour, and the post-war period has witnessed revolutionary changes in the practices of agriculture and in the attitude of the State, of which the student of agriculture might well desire some summary account.

The book is made up of 23 chapters and 10 appendices. The titles of the chapters are: The Manorial Systems of Farming; The Break-up of the Manor. 1300–1485; Farming for Profit: Pasture and Sheep Grazing. 1485–1558; The Reign of Elizabeth; From James I. To the Restoration. 1603–1660; The Later Stewarts and the Revolution. 1660–1700; Jethro Tull and Lord Townshend. 1700–1760; The Stock-breeder's Art and Robert Bakewell. 1725–1795; Arthur Young and the Diffusion of Knowledge. 1760–1800; Large Farms and Capitalist Farmers. 1780–1813; Open-field Farms and Pasture Commons. 1793–1815; The English Corn Laws; Highways; The Rural Population. 1780–1813; Agricultural Depression and the Poor Law. 1813–1837; Tithes; High Farming. 1837–1874; The Great Depression and Recovery. 1874–1912; The War and State Control. 1914–1918; Agricultural Legislation since the War; Small Holdings; Education and Research; and Technical Progress since the War.

The revision of the book has added to its attractiveness from the reader's point of view. This book should become a popular addition to the collection of our agricultural libraries and should prove to be a desirable item in other libraries as well.

Fifty Years of Field Experiments at the Woburn Experimental Station. By E. John Russell and J. A. Voelcker. Longmans, Green and Co., London, 1936. Pp. xvii + 392, plates 4, tables 246, figs. 42. Price $7.50.

The Rothamsted Experimental Station has created information of world-wide interest and importance. Students of agriculture outside England are not as familiar with the fine work that has been done at the Woburn Experimental Station as they are with that of the Rothamsted Station. The authors rendered a real service in writing a book dealing in an illuminating way with the genesis and development of the experimental work at Woburn.

The introductory statement was written by Sir John Russell, Director of the Rothamsted Station. It contains, among others, the following observa-

tion. "The results obtained on the light soil at Woburn fully confirmed those of the heavier soil at Rothamsted: they constitute an important part of the classic material relating to this problem. The controversy is now long ended and has passed into the domain of history."

The book consists of four parts. The first of these was written by J. A. Voelcker; the second, by W. G. Cochran; the third, by E. J. Russell, and the fourth, by E. M. Crowther. There are 22 chapters all told, aside from an appendix and index. The frontispiece represents a portrait of Dr. J. Augustus Voelcker. There are three other plates. There is much valuable statistical material, which is arranged in a way to meet the convenience of the reader. The book, as a whole, represents a substantial addition to our information on soils and crops.

Zoning. By EDWARD M. BASSETT. Russell Sage Foundation. New York. 1936. Pp. 275. Price $3.00.

The theory and practice of zoning have their friends as well as opponents. There will be no gainsaying the fact that intelligent persons, the country over, deplore the lack of definite and critical thinking in the development of our natural resources. The use of land is no exception. State and municipal legislation relating to zoning affects—indirectly, at least—the distribution of population, its density, and its demands upon land adjacent to urban centers as well as land located at a great distance. City zoning involves important implications as to land use in rural areas.

The book consists of a preface, 11 chapters, a bibliography, and two indices. The designations of the several chapters, as noted below, will serve to give the reader an understanding of the author's purpose in writing the book. The titles of the chapters are: Relation of Zoning to State Constitutions; State Enabling Acts for Zoning; The Adoption and Amendment of Zoning Ordinances; Zoning Districts; Nonconforming Buildings and Uses; Board of Appeals; Court Procedure; Criminal Proceedings; Contractual Relations; Definitions in the Ordinance; and Particular Buildings and Uses.

In general, the present work will serve to fix attention on a subject of timely interest.

Exploring for Plants. By DAVID FAIRCHILD. The Macmillan Company, New York, 1931. Pp. xx + 591, illus. 180. Price $3.00.

Since the early voyages of Columbus, North America has received many plant immigrants. Many of these are distinctly unwelcome guests. Our farmers and gardeners are carrying a heavy economic burden because of the numerous and troublesome weeds that have found their way to this country from foreign lands. There is, fortunately, a more pleasant side to the story of plant introduction. American agriculture has become enriched by numerous additions to our list of economic plants. Under the auspices of the United States Department of Agriculture and of other organizations, men of

courage and learning have searched far and wide for plants likely to give us higher yields per acre; greater resistance to disease; new types of food, fiber, and oil crops; new medicinal plants; and new ornamentals to delight the eye of the observer.

The author is one of the veteran explorers. He has brought to the United States many gifts, and to him we should not be wanting in gratitude. To quote a paragraph from his introduction:

> And in any case, this book does not constitute the only result of the years of travel and work which it describes; the really valuable results are growing up into trees and vines and useful plants, scattered from Panama to the Puget Sound. If any of them contributes a substantial benefit to the civilization of the coming centuries, the efforts of those who contributed to the Allison V. Armour Expedition, either in the field or as members of the staff of the Office of Foreign Plant Introduction of the United States Department of Agriculture, will not have been in vain.

The author and publishers have arranged the contents of the book in a most attractive form. The 43 chapters cover a wide range of subjects. The numerous illustrations will help the reader to visualize the author's personal experience and those of others. The reader will find in this book much that will bring him profit and pleasure.

The titles of the chapters are as follows: From Florida via Panama to Sweden; England's Great Garden and Arboretum; Dutch and Belgian Glimpses; Among the Herbaria and Gardens of France; Through France and Switzerland to Algeria; With Trabut in Algeria; The Oasis of Bou Saäda; Through Algeria to Morocco; From Oujda to Fez; Human Rabbit-warrens and Palaces of Fez; From Fez to Meknez and Rabat; Ouezzan and the Oued Korifla with Maire; The Garden of the Oudaias, the Maréchal and the Forest of Mamora; Casablanca and Marrakesh; Mogador and Agadir; On the Utowana to Teneriffe; The Island of Palma; Grand Canary and Lanzarote; The Balearic Islands; Equipping in Italy; Off to Ceylon; Collecting Days in Ceylon; Newara Eliya and Jaffna; Arriving in Sumatra; the Medan Institutions; In the Atchenese Highlands; Takengon and Het Bovenland; The Sibolangit Garden; Java at Last; The Bamboo Civilization of Java; Into Middle Java; East Java; Singapore, Switzerland, Sweden and America; Off for West Africa; The Gambia; French Guinea and Sierra Leone; The Liberian Republic; Fernando Po, Duala to Cameroon; The Cameroon; The Gold Coast; The Fouta Djallon Mountains; From Dakkar to Malaga; and Portugal and the End of the Cruise.

The Vegetable Gardener's How Book. By CHELSA C. SHERLOCK. The Macmillan Company, New York. 1937. Pp. xix + 286, illus. 55. Price $3.00.

The story of gardening for profit or pleasure has been told by many men in many books. The amateur as well as the business gardener is fortunate in having within reach old and new books on gardening. In recent years, much of distinct value has been added to the literature on the subject. The present

work is one of these. It would be appropriate to quote a short paragraph by the author, entitled *The Eternal Fitness of Things.*

'What is the greatest satisfaction you get out of your garden?' a friend asked the other day. I was stumped for a moment. But, do you know, I believe the biggest thing I get out of my garden is a sense of the eternal fitness of things? One cannot witness the riddle of the seasons, the unfolding of seeds into marvelous plants, the might and mystery of sunshine and rain upon senseless dust without coming closer to the Author of all Creation. Our strivings and our sense of importance fade when we dig in our gardens, for we turn up grains of pure gold and get back to the elemental things. With Emerson we come to say: 'All things matter, but nothing matters much'—except that there is Order back of it all and the highest attribute of intelligence is to know that it all matters some!

The book is divided into three parts, made up in all of 47 chapters and an appendix. For the reader's convenience, the topics are given below. He will find in it much of interest in Part I—The General Vegetable Garden, as well as in Part II—The Salad Garden, and Part III—the Fruit Garden. The home gardener should find a place for this work on his book shelf.

The chapters are entitled: Asparagus; Beans; Beets; Brussel Sprouts; Cabbage; Carrots; Cauliflower; Celery; Chard; Sweet Corn; Cucumbers; Eggplants; Kohlrabi; Melons; Onions; Parsnips; Peas; Peppers; Irish Potatoes; Sweet Potatoes; Pumpkins; Radishes; Rhubarb; Spinach; Squash; Tomatoes; Turnips; Salad Plants; Celeriac; Chicory; Collards; Corn Salad; Cress; Dandelions; Endive; Finochio; Horseradish; Kale; Lettuce; Parsley; Romaine Salad; Wong Bok (Pe-Tsai); Apples; Apricots; Blackberries; Cherries; Currants; Dewberries; Gooseberries; Grapes; Loganberries; Peaches; Pears; Plums; Quinces; Raspberries; and Strawberries.

The Study of the Soil in the Field. By G. R. CLARKE. The Clarendon Press, Oxford, 1936. Pp. 142, figs. 7, tables 3. Price $1.75.

This little book was published under the auspices of the Imperial Forestry Institute of the University of Oxford. Dr. C. G. T. Morison, of that University, has written a preface, from which the following may be quoted.

Soil science as it is understood to-day is a complex study involving many branches of fundamental science, and the problems presented for solution are such as can perhaps only be solved satisfactorily by a team consisting of physicists, chemists, geologists, botanists, and zoologists. There is, however, one aspect of soil study which was for many years sadly neglected, but which is of fundamental importance not merely in the problems of classification but also in elucidation of many of the problems of land utilization.

The book is made up, aside from Acknowledgement and Introduction, of five chapters and an index. The chapters are entitled, respectively, Soil Site-Characteristics; The Soil-Profile Pit; Soil-Sample Collection; Mapping of Soils; and Notes on Various Soil-Survey Systems. Of particular interest to the reader will be the contents of Chapters IV and V. The various soil survey systems are discussed helpfully in the fifth chapter.

The Earth Goddess. By G. HOWARD JONES. Longmans, Green and Co., London—New York—Toronto, 1936. Pp. VII + 205, illus. 7. Price $5.00.

The readers of this work will readily catch glimpses of far-away lands, of different dietaries, and different standards of living. To quote the author's statement in the preface:

> This book grew out of five years' observation of native peasant farming under primitive African conditions while the author was engaged on official agricultural work in Nigeria and Sierra Leone. There are so many features of West Coast farming that seem so new, and yet are so old when one comes to know them, that one's interest is aroused in searching for causes: and as the lines of enquiry necessarily broaden out it becomes obvious that West Coast agriculture is not only of technical interest to agriculturists, but closely concerns administrators, traders, and in fact all who have to deal with the West Coast. On a broader basis, too, West Coast agriculture undoubtedly has a contribution to make towards the methods to be used in developing tropical countries.

There is a very interesting frontispiece, designated: "Ala, The Earth Goddess of the Ibos." The work is made up of ten chapters and an index. The topics treated are: Ala, The Earth Goddess: and the Nature of Agriculture; Agricultural History of the West Coast: The Scientific and Economic Themes of the Fugue; Modern History: and The Social Theme; A Digression on Scale in Agriculture: Large Estates and The Petite Culture, with High and Low Farming; The Full Score Fugue and the Alternatives: Planter, Metayer and Small Grower; The Combination of Peasants: Agricultural Co-operation and its Potentialities; Schools and the Farmer; Rights and Duties in Holding Land; Fostering Progress among Small Growers: Model Farms, Extension Work and Agricultural Propaganda; A Recital: and Some Wider Considerations; Notes on the Bibliography.

Students of agriculture will recognize their debt to the author for having brought to their attention many facts that will be new to them and for having prepared a work that is readable and interesting.

Rothamsted Experimental Station Report for 1935. Gibbs & Bamforth, Ltd. St. Albans, England. Pp. 279.

Every student of research in agricultural science is familiar with the wide range of experimental work that is being done at the Rothamsted Station at Harpenden under the provisions of the Lawes Agricultural Trust. The present report reaches well back toward the beginning of modern agricultural research. It is scarcely necessary to quote from the introduction, which contains mention of some major historical facts relating to the activities at Rothamsted. For the convenience of the reader, it should be noted that the report deals with the staff and staff changes, with scientific papers published in 1935, with technical and other papers published in the same year, and with experimental data accumulated at Woburn, Rothamsted, and various experimental fields in 1934–1935. There will also be found in the report mention of the Imperial Bureau of Soil Science and its functions and activities.

The scope of the work at Rothamsted reflects the needs of agriculture, not only in England, but also in other parts of the British Empire. Important data are recorded on crops, plant nutrition, the composition of crops, of soils, soil micro-organisms, plant diseases, insects and insecticides, farm animals, and other topics in the field of agricultural experimentation. Reference is also made in the report to meteorological observations. Altogether, the report summarizes the results obtained in long term experiments and brings up to date information of wide interest.

Die Böden Des Deutschen Reiches und der Freien Stadt Danzig. By HERMANN STREMME. Justus Perthes, Gotha, Germany. 1936. Pp. 226, tables 14, and 1 colored map.

The student of soil mapping and classification will find much of distinct interest in this work on the soils of Germany and of the Free City of Danzig. The author is familiar with the methods of soil surveys, mapping, and classification in the United States and elsewhere and has been able to deal with his subject in the light of wide experience and knowledge. The present volume is a valuable addition to the literature on soil mapping and classification.

The nature of the treatment is indicated by the titles of the four chapters, and the series of tables, and the map. The titles of the chapters follow: Anfang, Anlass und gang der Bodenkartierung Deutschlands; Der Gesamtboden, seine Einteilung und Benennung; Das Gesamtbild der Karte; and Schlussbetrachtung die Böden Deutschlands im Rahmen der Gesamteuropäischen. The author has rendered a service to students of pedology.

Elements of Farm Management. By JOHN A. HOPKINS. Prentice-Hall, Inc., New York, 1936. Pp. xvii + 390, figs. 67, tables 49. Price $2.20.

To quote the author:

> The purpose of this book is to set forth some of the basic principles of production economics in a simple and realistic manner. *Elements of Farm Management* does not attempt to cover the entire field of production economics, but confines itself to a small number of fundamental principles. The principle of increasing and diminishing returns, the closely related principle of substitution are of primary importance. Their ramifications extend throughout the organization and management of the farm business.

The book consists of eight parts, designated, respectively: General Considerations; Organizing the Farm: Basic Principles; The Crop System; The Livestock System; Economizing Labor and Power; Summary of the Budget; Current Operation of the Farm; and External Relationships of the Farm Business. There are, in all, 25 chapters and an index. The designations of the several chapters follow: Economic Activity and Choosing an Occupation; Types of Farming; Specialization or Diversification; Obtaining the Use of a Farm; Organizing the Farm and the Farmer's Resources; Budgeting and Planning; The Principle of Diminishing Physical Output; The Principle of Diminishing Economic Returns; Selection of the Crops; Major and Minor

Rotations and Crop Records; Requirements in Crop Production; Purposes of Livestock in the Farm Organization; The Feed Supply and the Livestock System; Budgeting for the Livestock System; The Field Layout; Selecting Equipment to Economize Labor; Selecting the Type of Power—Horse or Tractor; Budgeting for General Expenses; Records to Check up on Farm Performance; Making Efficient Use of Labor; Checking up on Performance—Use of Records; Modifying the Budget and Allowing for Price Change; Co-operation in Current Farm Management; Financing the Farm Business; and The Farmer's Market Contacts. A list of references will be found at the end of each chapter.

Altogether, the author has brought up to date our conceptions of farm management. The work will be found timely and useful.

JACOB G. LIPMAN.

ERRATUM

SOIL SCIENCE, VOLUME 42

Behavior of Polyvalent Cations in Base Exchange, by J. E. Gieseking and Hans Jenny

P. 276. Last line, Li should read *Sr*.

ERRATA

SOIL SCIENCE, VOLUME 43

A Pedologic Study of Some Soils in New Jersey, by J. S. Joffe

P. 227. Second line from bottom, orogenic should read lithogenic.

P. 230. Tenth line from bottom, lower should read higher.

THE INFLUENCE OF LEAD COMPOUNDS ON THE GROWTH OF BARLEY[1]

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INTRODUCTION

In a recent investigation of the influence of lead arsenate spray accumulations on orchard soils, it was thought advisable to determine the separate effects of lead and arsenic on plant growth.

Literature on the influence of lead on plant growth is limited, and large differences of opinion exist in the published statements. Greisenegger (4), working with applications of lead compounds to the soil, as well as Devaux (3) and Nobbe, Baessler, and Will (11), who grew plants in culture solutions to which lead compounds had been added, observed no influence of lead on plant growth. Bonnet (2), Hammett (6), Haselhoff, Fluhrer, and Haun (7), Lundegardh (10), and Knop (8) found detrimental effects on plant growth in culture solutions containing lead, as did Griffith (5) and Lipman (9) in soils containing lead. Contrary to this, Berry (1) and Scharrer and Schropp (12), working with culture solutions, and Stoklasa (14), Stutzer (15), and Voelcker (17), with soils, reported stimulation of plant growth by additions of small amounts of lead. Because of these differences in results and of the possible importance of lead in the toxic effects resulting from lead arsenate spray accumulations in the soil, the influence of lead on the growth of barley was investigated.

METHODS OF INVESTIGATION

A series of pots containing soil taken from a field in the Yakima orchard district, which had not been subjected to a spray program, were treated with various amounts of lead nitrate and lead carbonate. Two different types of lead compounds were used in order to ascertain any effect that might result from variations in solubility of the lead compounds. The lead nitrate, prepared in a water solution, and the lead carbonate, in a water suspension, were mixed with the air-dried soil in the pots in various amounts corresponding

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to probable accumulations in the soil under field conditions following different spraying practices.

The treated soils were brought to optimum moisture conditions and permitted to stand for three days to allow sufficient time for the attainment of approximate equilibrium conditions between the lead compounds and the soil. It was found in a previous experiment (16) that approximate equilibrium conditions were established within a few hours, though a slight fixation of lead by the soil continued during the growing period of the crops. Enough

TABLE 1

Recovery of 0.1 N ammonium nitrate soluble lead from 2 different soils by different methods

SOIL	TREATMENT WITH $Pb(NO_3)_2$	0.1 *N* NH_4NO_3 SOLUBLE LEAD RECOVERED		
		Diphenylthiocarbazone colorimetric	Sodium sulfite colorimetric	Chromate gravimetric
	p.p.m. (PbO)	*p.p.m.* (PbO)	*p.p.m.* (PbO)	*p.p.m.* (PbO)
A	60	0.36	0.275	.....
A	500	1.25	1.275	.....
A	1000	5.99	.....	5.75
A	3000	15.00	.....	15.00
B	60	0.90	0.775	.....
B	500	4.00	4.275	.....
B	1000	5.66	.....	5.00
B	3000	18.15	.....	17.50

TABLE 2

Influence of different extracting agents on the amounts of readily soluble lead in two different soils

SOIL	TREATMENT WITH $Pb(NO_3)_2$	SOLUBLE LEAD			
		0.1 *N* NH_4NO_3	0.1 *N* NH_4Ac	.005 *N* HNO_3	H_2O
	p.p.m. (PbO)	*p.p.m.* (PbO)	*p.p.m.* (PbO)	*p.p.m.* (PbO)	*p.p.m.* (PbO)
A	60	0.36	0.31	0.30	0.30
A	500	1.25	1.24	1.25	1.24
A	1000	5.00	6.90	6.25	5.62
A	3000	15.00	15.50	15.50	14.50
B	60	0.94	.....	.....	0.90
B	500	4.17	.....	4.12	4.00
B	1000	5.00	5.60	5.00	5.50
B	3000	18.15	18.75	18.39	18.00

nitrogen was added to the check and lead carbonate treated pots to equal the nitrogen added in the form of lead nitrate to pot 3, to which 120 p.p.m. of PbO as lead nitrate had been added. This amount represented the average of the lead nitrate treated pots. Soil samples were taken for analysis from all the pots, which were then planted to barley and placed in the greenhouse, where optimum growing conditions were maintained. The plants were harvested at the milk stage of maturity, the tops and the roots being taken separately. Samples of the soil were also obtained at this time. The experi-

ment was repeated, following the same procedure, except that duplicate treatments were used, and sufficient nitrogen in the form of ammonium nitrate was added to all pots to equal the nitrogen added in the pot containing the highest quantity of lead nitrate, which was 500 p.p.m. of PbO as $Pb(NO_3)_2$.

Two different soils were treated with various quantities of lead nitrate, and samples of the treated soils used to check the colorimetric diphenylthiocarbazone method (18) for lead against the colorimetric sodium sulfite method (18), or the gravimetric chromate method (13, p. 279–280), depending on the quantity of lead present in the soil. The results of the three different methods on the amounts of lead extracted by 0.1 *N* ammonium nitrate in a 1:5 ratio of soil to solution are comparable, as is shown in table 1. It was decided to use the diphenylthiocarbazone method because of its adaptation for quantitative analysis of minute quantities of lead.

Samples of these same treated soils were used to compare different solvents as extracting agents for readily soluble lead. The results, which are given in table 2, show no appreciable variation in the amounts of lead extracted by these solutions. Because of the advantage of having the lead in the nitrate form when the diphenylthiocarbazone method is used, and the desirability of having the soil in a flocculated condition to speed up filtration, ammonium nitrate was selected as the extracting agent for the soils.

PROCEDURE

The soil samples taken at the beginning and end of the experiment were extracted with 0.1 *N* ammonium nitrate solution, using a 1:5 ratio of soil to solution, and the lead in the filtrate was determined by the diphenylthiocarbazone method as reported in the procedure of a previous paper (16). The term soluble lead as used in this paper refers to the lead which is soluble in a 0.1 *N* ammonium nitrate solution. Both the roots and tops of the barley were digested in 1:1 HCl and $KClO_3$, as recommended by Scott (13, p. 51), and the lead determined in the filtrate. The roots, which were taken separately, were thoroughly cleaned by washing before digesting.

EXPERIMENTAL RESULTS

Since the soluble lead content of a number of soils investigated previously (16) was found to be very slight even in orchard soils which had received large quantities of lead arsenate spray, various amounts of lead, ranging from 60 to 240 p.p.m. of PbO as $Pb(NO_3)_2$ and from 1,000 to 3,000 p.p.m. PbO as $PbCO_3$, were added to the soil samples used in this experiment. The soil treatments and the amounts of soluble lead recovered from the soil at planting time and after the plants were harvested are recorded in table 3. For the subsequent repetition of the experiment, they are shown in table 4. In this experiment, the treatments were in duplicate and the check pots in triplicate. Treatments of 500 p.p.m. of PbO as $Pb(NO_3)_2$ and as $PbCO_3$ were included. The time of growth of the initial experiment was from February 7, 1936, to May 7,

1936, whereas that of the second experiment was from August 20, 1936, to October 31, 1936.

The results show that nearly all the lead had been fixed by the soil within a few days, leaving only minute quantities of it in the soluble form at planting time and still smaller amounts at the time of harvest, indicating that a very

TABLE 3

Amounts of soluble lead recovered from the soil at planting time and at harvesting time in experiment started Feb. 7, 1936

EXPERIMENT NUMBER	TREATMENT	AMOUNT OF SALT ADDED	READILY SOLUBLE PbO	
			Planting time	Harvesting time
		p.p.m. (PbO)	*p.p.m.*	*p.p.m.*
1	Check	0	trace	trace
6	Check	0	trace	trace
2	$Pb(NO_3)_2$	60	0.093	0.042
3	$Pb(NO_3)_2$	120	0.160	0.047
4	$Pb(NO_3)_2$	180	0.210	0.065
5	$Pb(NO_3)_2$	240	0.370	0.140
7	$PbCO_3$	1000	1.350	0.050
8	$PbCO_3$	2000	2.400	0.540
9	$PbCO_3$	3000	3.250	1.350

TABLE 4

*Amounts of soluble lead recovered from the soil at planting and at harvesting time in experiment started Aug. 20, 1936**

EXPERIMENT NUMBER	TREATMENT	AMOUNT OF SALT ADDED	READILY SOLUBLE PbO	
			Planting time	Harvesting time
		p.p.m. (PbO)	*p.p.m.*	*p.p.m.*
1	Check	0	trace	trace
2	$Pb(NO_3)_2$	60	0.161	0.024
3	$Pb(NO_3)_2$	120	0.336	0.026
4	$Pb(NO_3)_2$	180	0.377	0.049
5	$Pb(NO_3)_2$	240	1.750	0.121
6	$Pb(NO_3)_2$	500	2.250	0.202
7	$PbCO_3$	500	2.020	0.201
8	$PbCO_3$	1000	2.450	0.395
9	$PbCO_3$	2000	2.890	0.471
10	$PbCO_3$	3000	3.230	1.109

* Results given are average of duplicate treatments.

slow fixation action of the soil on the lead had continued during the growing period. The amounts of lead removed by plant growth were insufficient to account for the change in concentration of readily soluble lead. Regardless of the form in which the lead was added to the soil, the amount of soluble lead recovered from it increased in proportion to the amounts present in the com-

pounds originally added. This is further substantiated by the addition of equal quantities of PbO as nitrate and carbonate to two separate soil samples in the repetition of the experiment. The amounts of soluble lead recovered from these soils are identical. A comparison of the concentrations of soluble lead present in the soils at harvest time with those present at planting time

TABLE 5

Growth and lead content of barley planted Feb. 7, 1936

POT NO.	DRY WEIGHT OF PLANT		DRY WEIGHT OF TOPS		PbO IN TOPS	DRY WEIGHT OF ROOTS		PbO IN ROOTS
	Actual	Relative	Actual	Relative		Actual	Relative	
	gm.	*per cent*	*gm.*	*per cent*	*p.p.m.*	*gm.*	*per cent*	*p.p.m.*
1	3.860*	100.00	2.720	100.00	0.00	1.140	100.00	0.0
6	3.692*	100.00	2.650	100.00	0.00	1.042	100.00	0.0
2	3.610	95.26	2.000	74.50	5.40	1.610	147.60	177.0
3	4.172	110.80	2.430	90.50	2.92	1.742	159.75	205.5
4	6.795	183.40	4.500	167.70	2.40	2.295	201.36	94.2
5	6.125	165.00	4.260	158.75	2.53	1.865	171.00	96.0
7	4.165	110.60	2.620	97.18	2.71	1.545	141.70	488.0
8	5.016	133.95	3.301	124.95	4.33	1.715	156.30	502.0
9	4.665	124.45	3.205	119.38	3.37	1.460	133.85	1475.0

* The average weight of check plots was given a value of 100.

TABLE 6

*Growth and lead content of barley planted Aug. 20, 1936**

POT NO.	DRY WEIGHT OF PLANT		DRY WEIGHT OF TOPS		PbO IN TOPS	DRY WEIGHT OF ROOTS		PbO IN ROOTS
	Actual	Relative	Actual	Relative		Actual	Relative	
	gm.	*per cent*	*gm.*	*per cent*	*p.p.m.*	*gm.*	*per cent*	*p.p.m.*
1	5.637†	100.00	3.823	100.00	trace	1.814	100.00	5.1
2	7.249	128.60	4.975	130.10	0.77	2.274	125.20	154.1
3	5.833	103.30	4.095	107.10	0.80	1.738	95.80	308.2
4	6.751	119.80	4.813	126.00	1.28	1.938	106.90	205.5
5	5.454	96.80	3.869	101.20	2.05	1.585	87.40	231.0
6	5.361	95.20	3.658	95.60	2.57	1.603	88.45	617.0
7	6.593	117.00	4.413	115.30	1.28	2.180	120.20	154.1
8	7.051	125.10	5.135	134.20	1.80	1.916	105.60	360.0
9	6.879	122.10	4.934	129.10	2.57	1.945	107.30	566.0
10	5.732	101.45	4.120	107.65	3.08	1.612	89.00	808.0

* Results given are the average of duplicate treatments.

† The average weight of check plots was given a value of 100.

confirms previous observations and suggests that a slow, continued fixation of the lead takes place as time progresses. Actual quantities of soluble lead recovered from the soil in the two experiments, both at planting and at harvest time, show that the fixation of the lead by the soil is a specific action depending on the properties of the soil used. Further experimentation on this action is to be undertaken.

Although only minute quantities of soluble lead were recovered from the soil, the growth of barley in response to the different treatments with lead compounds varied considerably, as can be seen from the data in tables 5 and 6. The appearance of the plants just before they were harvested is shown in plates 1 and 2. Although the total dry weights of the plants vary considerably, no toxic action was evident regardless of the amount of lead applied or the soluble lead content of the soil. It appears, however, that barley is sensitive to the presence of lead in the soil, and that this sensitivity is manifested in the form of a stimulation in growth. This stimulation seems to be more pronounced under certain concentrations of soluble lead in the soil. Even though the individual results show wide variation, plotting the calculated averages of the dry weights of the tops and roots against the soluble lead content of the respective soils, as shown in figure 1, indicates that a concentration of soluble lead between 0.1 and 0.4 p.p.m. of PbO has a tendency to exert the greatest stimulation. The stimulating effect was still manifested when an application was made at the rate of 7,190 pounds of lead carbonate per acre based on 2,000,000 pounds of soil, which probably exceeds any amount that is likely to accumulate in the soil as a result of a heavy spraying schedule carried on over a period of years.

The results obtained with barley in the presence of soluble lead in the soil are similar to those of Scharrer and Schropp (12) who, using lead acetate in sand and solution cultures, found the greatest growth when the lead content in the form of lead acetate was between 0.02 and 1 p.p.m. They observed no detrimental effects until a concentration of 100 p.p.m. of lead as lead acetate was used. The germination of the seeds they used seemed to be stimulated by smaller amounts of lead than was the plant growth. This greater stimulation of germination than of subsequent growth has also been observed by Voelcker (17).

The data on plant analysis in tables 5 and 6 show that lead was present in both the tops and the roots of the barley. This indicates that lead was absorbed by the roots, and a small part of it translocated to the aerial parts of the plant. Even though the amounts of lead translocated to the aerial parts of the plant are small, they may be significant from the nutritional point, if it is considered that the values obtained approach the tolerance limit of lead, 0.018 grains per pound, established by the Food and Drug Administration. The amounts of lead absorbed by the roots were high, ranging from 100 to 800 p.p.m. of PbO in the dry root tissues. Hammett (6) also found a high concentration of lead in the roots of plants grown in water cultures containing soluble lead. In a microscopic study of the root tissues and cells, Hammett found that the lead was deposited mainly in the division zones of the roots. The roots of the barley grown in all of the lead treated soils in the experiments here discussed appeared of a darker brown than those grown in the check soil.

The amounts of lead absorbed by the growing barley varied from treatment

to treatment, but in general increasing rates of application of lead compounds, which resulted also in correspondingly greater amounts of soluble lead in the soil, caused a general increase in the amounts of lead absorbed by the plants in both tops and roots. The data in table 6 for pots 6 and 7 are of interest. These pots received equal amounts of lead, one in the nitrate form and the other in the carbonate form. Although the soluble lead content of the two pots was similar, the barley grown in the nitrate treated soil absorbed greater quantities of lead. Thus, although the anion had no effect on the solubility of the lead compound in the soil, there is some indication that the amount of lead absorbed by the plant may be influenced by it.

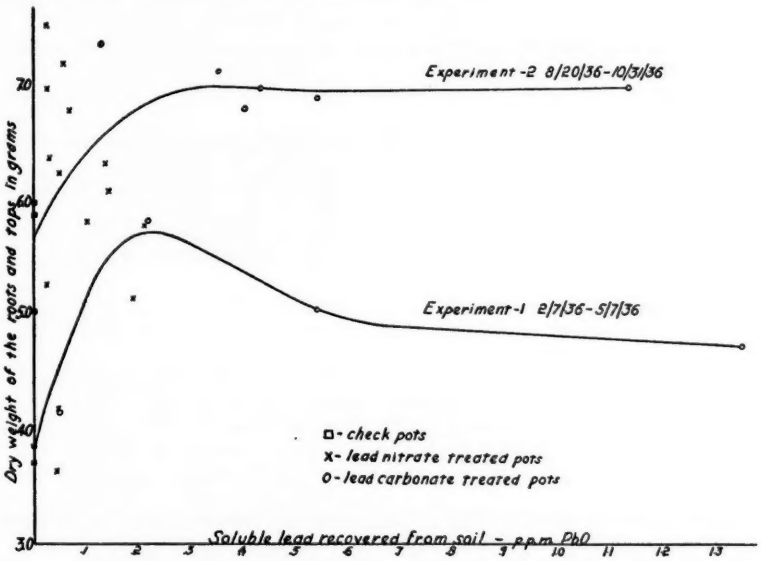

FIG. 1. DRY WEIGHTS OF THE TOPS AND ROOTS OF THE INDIVIDUAL PLANTS PLOTTED AGAINST THE SOLUBLE LEAD CONTENT OF THE SOIL

SUMMARY

Evidence is shown by the results obtained in this study that because of the high fixing power of the soils used, large quantities of lead could be added without harmful effects. When amounts at the rate of 7,190 pounds of lead carbonate per acre were used, no detrimental effects on the growth of barley were observed.

The tendency was for the growth of barley to be stimulated by minute quantities of soluble lead in the soil. A relationship appears to exist between the growth stimulation and the soluble lead content of the soil, with a tendency for maximum stimulation to occur when the concentration of soluble lead ranges between 0.1 to 0.4 p.p.m. PbO.

Lead was found in the plants in both tops and roots, the concentration in the latter being notably higher than in the tops. The tendency of the plants was to absorb greater quantities of lead with increasing concentrations of soluble lead in the soil.

REFERENCES

(1) BERRY, R. A. 1924 The manurial properties of lead nitrate. *Jour. Agr. Sci.* 14: 58–65.
(2) BONNET, E. 1922 Action of soluble lead salts on plants. *Compt. Rend. Acad. Sci.* [Paris] 174: 488–491.
(3) DEVAUX, H. 1901 Fixation of metals by cell walls. *Compt. Rend. Acad. Sci.* [Paris] 132: 717.
(4) GREISENEGGER, K. J. 1915 Lead nitrate as a catalytic fertilizer for sugar beets. *Österr.-Ungar. Ztschr. Zuckerindus. u. Landw.* 44: 91–96.
(5) GRIFFITH, J. J. 1919 Influence of mines upon land and live stock in Cardiganshire. *Jour. Agr. Sci.* 9: 366–395.
(6) HAMMETT, F. S. 1928 Studies in the biology of metals, I & II. *Protoplasma* 4: 183–191.
(7) HASELHOFF, E., FLUHRER, K., AND HAUN, F. 1923 Experiments with caustic materials. *Landw. Vers. Sta.* 100: 59–78.
(8) KNOP, J. 1885 Berichte über die Verhandlungen der kgl. sachgischen Gesellschaft der Wissenschaften. *Math. Phys. Kl.* 37: 50–51.
(9) LIPMAN, C. B., AND BURGESS, P. S. 1914 Effect of copper, zinc, iron and lead salts on ammonification and nitrification in soils. *Univ. Calif. Pub. Agr. Sci.* 1: 127–139.
(10) LUNDEGARDH, H., BURSTROM, H., AND EKSTRAND, H. 1930 The action of inorganic disinfectants on germination and germ growth of grain. *K. Landtbr. Akad. Handl. och Tidskr.* 69: 602–632.
(11) NOBBE, F., BAESSLER, P., AND WILL, H. 1884 Poisonous effects of arsenic, zinc, and lead on vegetable organisms. *Landw. Vers. Sta.* 30: 381.
(12) SCHARRER, K., AND SCHROPP, W. 1936 Über die Wirkung des Bleis auf das Pflanzenwachstum. *Ztschr. Pflanzenernähr., Düngung, u. Bodenk.* 43: 34–43.
(13) SCOTT, W. W. 1927 Standard Methods of Chemical Analysis, ed. 4, vol. 1. New York.
(14) STOKLASA, J. 1913 Influence of uranium and lead upon vegetation. *Compt. Rend. Acad. Sci.* [Paris] 156: 153–155.
(15) STUTZER, A. 1916 The action of lead as a stimulant for plants. *Jour. Landw.* (64) 1–2: 1–8.
(16) VANDECAVEYE, S. C., HORNER, G. M., AND KEATON, C. M. 1936 Unproductiveness of certain orchard soils as related to lead arsenate spray accumulations. *Soil Sci.* 42: 203–215.
(17) VOELCKER, J. A. 1914 The Woburn pot culture experiments. *Jour. Roy. Agr. Soc. England* 75: 306–322.
(18) WICHMANN, H. J., MURRAY, C. W., HARRIS, M., CLIFFORD, P. A., LOUGHREY, J. H., AND VORHES, JR., F. A. 1934 Methods for the determination of lead in foods. *Jour. Assoc. Off. Agr. Chem.* 17: 108–135.

PLATE 1

FIG. 1. Lead nitrate treated pots. May 7, 1936 (1) check, (2) 60 p.p.m. PbO, (3) 120 p.p.m. PbO, (4) 180 p.p.m. PbO, (5) 240 p.p.m. PbO.

FIG. 2. Lead carbonate treated pots. May 7, 1936 (6) check, (7) 1,000 p.p.m. PbO, (8) 2,000 p.p.m. PbO, (9) 3,000 p.p.m. PbO.

FIG. 1

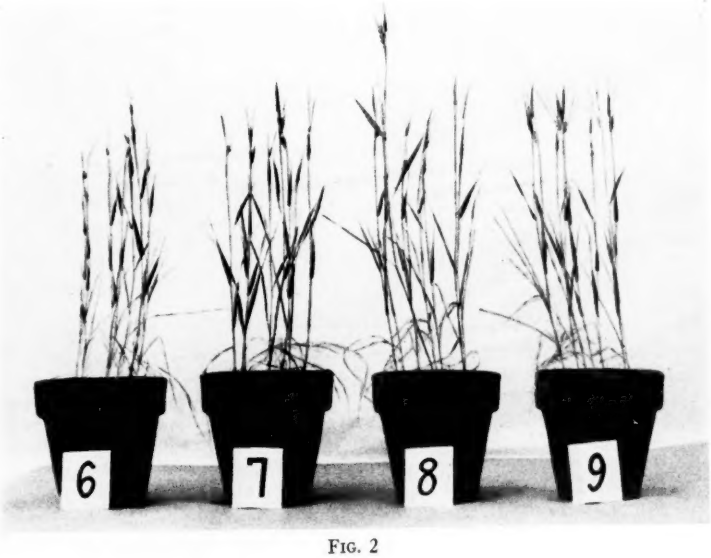

FIG. 2

PLATE 2

FIG. 1. Lead nitrate treated pots. Oct. 31, 1936 (1) check, (2) 60 p.p.m. PbO, (3) 120 p.p.m. PbO, (4) 180 p.p.m. PbO, (5) 240 p.p.m. PbO.

FIG. 2. Lead carbonate treated pots. Oct. 31, 1936 (1) check, (6) 500 p.p.m. PbO, (7) 1,000 p.p.m. PbO, (8) 2,000 p.p.m. PbO, (9) 3,000 p.p.m. PbO.

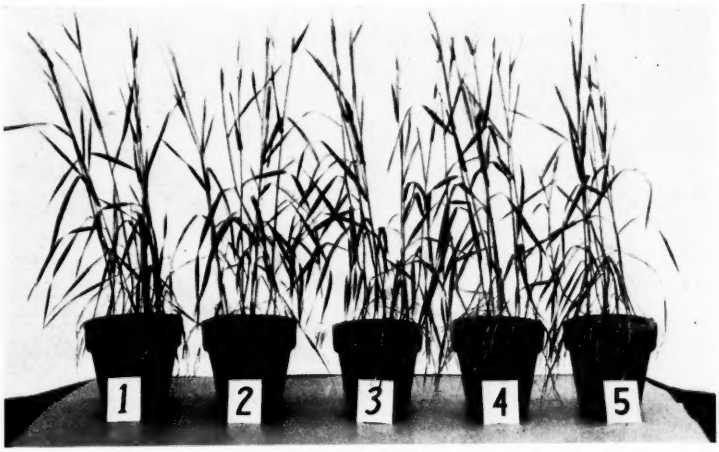

FIG. 1

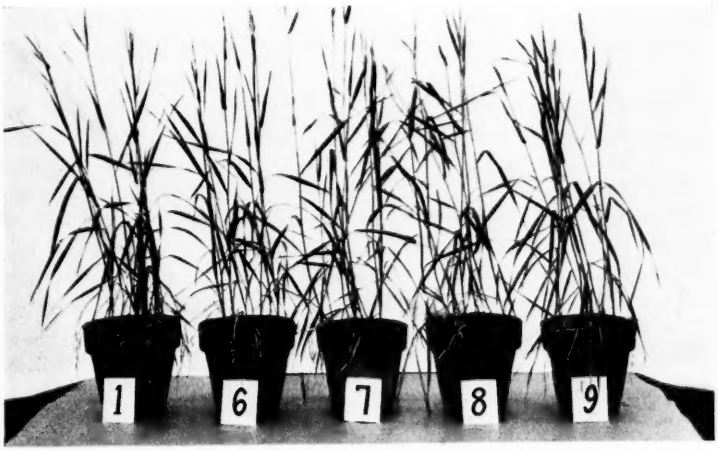

FIG. 2

SOIL ORGANIC MATTER AND POROSITY OF AN ORCHARD SOIL UNDER DIFFERENT CULTURAL SYSTEMS

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Received for publication February 11, 1937

The purpose of this study was to determine the content of organic matter in orchard soils which have been under three systems of culture: namely, tillage with cover crops, mulch, and bluegrass sod. A number of questions present themselves to the horticulturist in attempting to determine the best soil management program. Two of them are: (a) Which system best prevents loss of organic matter from the soil either through erosion or excessive oxidation and provides a new supply in increasing ratio? (b) Which system conserves the moisture supply, provides nitrates and other essential nutrients, and results in adequate aeration and favorable soil structure?

The investigations here reported are continuations of studies begun in 1935, one phase of which has already been considered (4).

ORCHARDS USED AS SOURCES OF SAMPLING MATERIAL

Two orchards at the Ohio Station were used as sources of samples for determining the organic matter content of the soil. These were selected because they have been under definite systems of culture for a comparatively long time. One is known as Orchard A, and the other as Orchard C.

Orchard A comprises 7 acres with the permanent trees set 33 feet apart and was planted in the spring of 1893. For 6 years, the orchard was cultivated, and then it was seeded to grass, and the soil has been undisturbed for the last 37 years. Since it was seeded down, a heavy mulch has been maintained around the trees. As the diameter of the heads of the trees increased in size, the width of the mulch was extended as far as the outermost branches, or a little farther. Wheat straw has been used most extensively for mulch, although oat straw, damaged alfalfa, timothy, soybean straw, sweet clover, grass clippings, and leaves have all been used to some extent. For the purposes of this study, it would have been preferable to have used either a non-legume or a legume, entirely, as the mulch material, preferably the latter. The exact amount used per unit area has not been recorded, but it has been ample to prevent any growth of grasses beneath the trees. Usually, the loose material has been several inches deep over the mulched area.

In 1927, the treatment of trees in one block of Orchard A was changed from the sod-mulch treatment to cultivation. Since then, this block has been cultivated and sown to cover crops of soybeans and rye.

That the sod-mulch system of culture has been satisfactory is evidenced from its productivity. The average yield of 15 of the better known varieties was 15.5 bushels per tree for a 26-year period (1910–1935). This is equivalent to an average annual yield of 620 bushels per acre, at the distance these trees were planted. Both the soil and site, as well as the cultural system followed, are considered favorable.

It may be mentioned, incidentally, that at no time has the foliage of the trees been yellowish in color or have the trees shown other evidences of nitrogen deficiency, such as would be probable if an annual crop was mulched with fresh straw.

Orchard C was planted in 1915, and half the trees have been continuously cultivated with cover crops of soybeans for the summer and rye for the winter. There has been some variation from this in recent years, when oats and Sudan grass have been used. The other half of the orchard was planted in sod, and the mulch system was begun at once. Aside from these two systems of culture, the orchard practices have been the same in both blocks.

The growth and yield of the trees in both blocks have been above the average for this region, although the records of total yield are slightly in favor of tillage, and the growth behavior is superior under the mulch. Recently, particularly during the years of extreme drought, the yields of the mulched trees have equaled, or surpassed, those of the tilled ones. The sod area used in the determinations here reported was adjacent to that of the mulched, or tilled, area and on the same soil type.

The soil in general is classified as the Wooster silt loam, and the tree roots in it are well distributed to a depth of 5 to 6 feet.

SOIL ORGANIC MATTER

Methods used. The soil organic matter determinations were made in August and September of 1935, and in August, September, and October of 1936. Since the determinations made in 1935 checked very closely with those secured at the same locations in 1936, the means only are given in the data (table 1).

Several methods for determining the soil organic matter were used experimentally in these studies. The one, however, which proved the most satisfactory in 1935 was that of chromic acid, reported by Schollenberger (5), with the modifications in amount of soil used and time of heating suggested by Degtjareff (3). A later recommendation by Schollenberger (6), to use one of several substances to obtain a more definite end point, was adopted. For this purpose, 85 per cent phosphoric acid was used, as described by him.

The modifications of Schollenberger's method suggested by Allison (1) were found to be quite satisfactory and were used in 1936, principally because of increased convenience and rapidity. The methods used in obtaining the results given in table 1 checked very closely with each other.

At least five determinations were made on each soil sample in 1935 and at least three in 1936. The average carbon content was then used in calculating

the percentage of organic matter in the sample. The above method of determination of organic matter was not as exact as certain other methods, but it was satisfactory for the purpose of these studies, where relative values are of primary concern.

In securing the soil for organic matter determinations, the mulch was completely removed, and a trench was dug so that one side was vertical. Then a sample of about 400 gm. of soil was removed from the side of the trench at four successive 2-inch levels.

TABLE 1

Soil organic matter determinations in orchards in sod, mulch, and cultivation

NO. OF TREE NEAR WHICH SAMPLE WAS TAKEN	MULCH				SOD				CULTIVATION			
	Depth (inches) of layer sampled				Depth (inches) of layer sampled				Depth (inches) of layer sampled			
	0–2	2–4	4–6	6–8	0–2	2–4	4–6	6–8	0–2	2–4	4–6	6–8
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Orchard A												
197	3.73	2.17	1.66	0.82	3.29	1.78	1.48	0.80				
327	5.89	3.33	1.65	0.93	4.52	2.12	1.55	1.04				
329	3.66	1.82	1.46	1.03	2.69	1.60	1.19	0.72				
289	3.91	2.04	1.65	1.14	3.60	2.08	1.01	0.77				
301*									1.87	1.64	1.45	0.94
Orchard C												
4/2	4.41	2.92	2.42	1.42	2.91	2.21	1.92	1.40				
4/5	4.80	3.40	2.01	1.35	4.52	3.30	1.91	1.31				
3/2	4.36	3.20	2.10	1.22	3.86	3.14	2.10	1.30				
3/5	5.06	2.17	1.55	1.02	4.60	2.33	1.04	0.85				
2/1									2.07	1.71	1.25	0.84
1/5									1.64	1.74	1.73	0.78
2/1									1.91	2.30	1.94	1.00
2/4									2.12	2.14	2.01	1.26

* Previously in sod, cultivated since spring of 1927.

The soil from the sod plots was taken after the sod had been pulled away. By use of this method, the removal of from 1 to 1½ inches of the top soil was unavoidable. This should be considered in referring to the data presented with reference to percentage of organic matter under sod. If it had been possible to measure accurately all the organic matter, not including roots, from the surface of the soil, very likely it would have been higher under sod than is given in the data. The soil under the sod was taken as near as possible to that under the mulch; usually not more than 4 to 6 feet away.

In the cultivated plot, the samples were taken from positions as comparable as possible, from the standpoint of soil character, to those from the mulched and sodded areas. They, too, were taken at successive 2-inch levels from the surface of the soil.

Results. The data on content of soil organic matter under various cultural treatments (table 1) indicate, first, that under all treatments the organic matter decreases from the surface downward; second, that there is no great difference in organic matter under the sod and mulch for, although the mulched soil is consistently higher in the first 4 inches, it must be noted that about an inch of the top soil had been removed with the sod. Probably, there was actually little or no difference in the amount of organic matter under mulch and that under sod. Third, the greatest and most significant difference is the low amount of organic matter in the cultivated soil in comparison with the other two treatments.

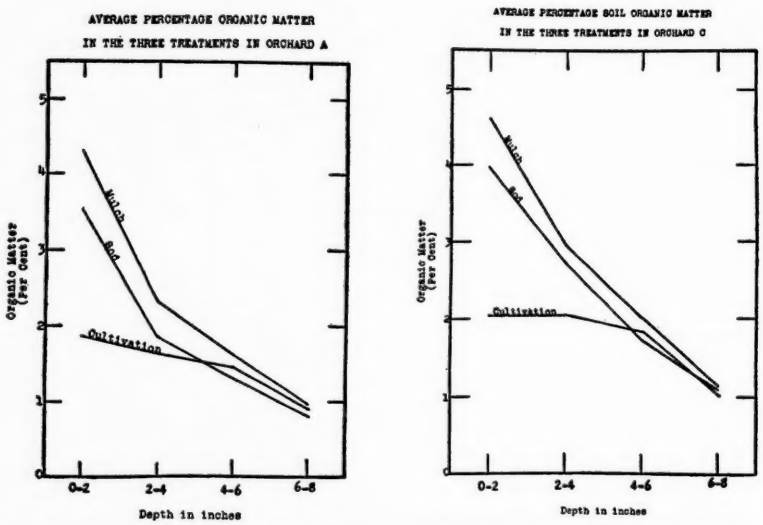

FIG. 1. AVERAGE SOIL ORGANIC MATTER CONTENT (C × 1.724) AT VARIOUS DEPTHS UNDER SOD, MULCH, AND CULTIVATION (p. 5, 6)

There is considerable variation in the percentage of soil organic matter obtained at various locations in the orchard. This again shows the importance of securing comparable samples from several locations, as well as obtaining fairly large samples (about 400 gm.) from each location from which to determine the carbon content.

The content of soil organic matter, as determined by this method (carbon × 1.724), is not considered high under any of the treatments. The first 4 inches under mulch and sod has been described as "humus-containing soil," whereas the second 4 inches has been described as "humus-poor soil."

It has often been assumed that mulches greatly increase the organic matter of the soil. This may not be true, even though it is higher under the mulch, for no doubt much of this difference between the cultivated and the mulched or

sod plots has been due to a decrease of organic matter under cultivation. This seems to be true even though cover crops have been continually grown and disced under in the cultivated plots.

Figure 1 shows the relative average organic matter content under the three treatments. The figures relative to sod and mulch, however, are limited in their value, since the means of all locations are averaged. There is so much difference between results from the different positions that each one should be considered separately or in comparison to other samples secured near the same tree. The data given in table 1 are much more significant. Figure 1, however, does show that below 5 to 6 inches the soil organic matter content is about the same under all three treatments.

Soil samples obtained from a forest of catalpa near Orchard A, in which the soil had not been disturbed since 1905, showed that the mulched orchard plots were slightly higher in organic matter. Thus, the forest plot contained much more organic matter than the cultivated orchard plots. The average in the forest soil was 3.57, 2.28, 1.56, 0.97, respectively, in each 2-inch level from the top of the soil.

SOIL POROSITY

Methods used. In order to determine the porosity of the soil under the various treatments, the volume-weights and the rapidity of water absorption were measured. The methods used were similar to those used and described by Auten (2) in his study of porosity and water absorption in forest and field soils.

In securing soils for volume-weight (or apparent specific gravity), a galvanized tube 2½ inches in diameter and 12 inches long was driven into the soil to a depth of 4 inches. Thus 321.9 cc. of soil was obtained. In the case of the mulch and sod, the surface litter was carefully removed from the surface of the soil. The sampling locations were selected so as to secure as uniform soil conditions as possible. The relative weights were determined on the air-dried soil.

In measuring water absorption, cylinders 2 inches in diameter and 12 inches long were driven into the soils to a uniform depth of 3.5 cm. The cylinders were kept full for 2 hours by pouring water into each from a container of known volume. The amount of water remaining in each container was then added to the known volume of water in the cylinder, and the sum was subtracted from the original amount. The figure obtained represented the quantity of water absorbed by the soil. From this was calculated the cubic centimeters absorbed per minute during the two hours.

These water absorption determinations were made at a time when the moisture content of all the soils was at about field capacity. If the soils had been lower in moisture content, they would probably have absorbed the water much more rapidly.

It is not meant to imply that this method of measuring rates of water ab-

sorption is accurate under all conditions and exactly comparable to rainfall absorption. It must be considered from a relative viewpoint and as another measurement of relative soil porosity.

Results. The mean weights of equal volumes of the Wooster silt loam soil to a depth of 4 inches indicate relatively small, but significant, differences

TABLE 2

Weights of constant soil volumes (321.9 cc.) in Orchard A

MEANS OF 10 DETERMINATIONS AND STANDARD DEVIATION

Under mulch		Under sod		Under cultivation	
gm.	*S.D.*	*gm.*	*S.D.*	*gm.*	*S.D.*
397.5*	15.02	415.5*	11.34	434.5*	14.05

	DIFFERENCE BETWEEN TREATMENTS		APPROXIMATE ODDS FOR SIGNIFICANCE OF DIFFERENCE†
	gm.	*S.D.*	
Mulch—sod	18.0	5.9	370 to 1
Mulch—cultivation	37.0	6.5	Over 9999 to 1
Sod—cultivation	19.0	5.7	Over 999 to 1

* Weights given in this table are equivalent in terms of pounds per cubic foot to the following: under mulch—77.04; under sod—80.56; under cultivation—95.79.

† From Pearl, Medical Biometry and Statistics.

TABLE 3

Weights of constant soil volumes (321.9) cc. in Orchard C

MEANS OF 10 DETERMINATIONS AND STANDARD DEVIATION

Under mulch		Under sod		Under cultivation	
gm.	*S.D.*	*gm.*	*S.D.*	*gm.*	*S.D.*
387.0	16.40	406.0	15.80	427.5	13.54

	DIFFERENCE BETWEEN TREATMENTS		APPROXIMATE ODDS FOR SIGNIFICANCE OF DIFFERENCE*
	gm.	*S.D.*	
Mulch—sod	19.0	7.20	110 to 1
Mulch—cultivation	40.5	6.7	Over 9999 to 1
Sod—cultivation	21.5	6.6	800 to 1

* From Pearl, Medical Biometry and Statistics.

between the treatments (table 2). The most compact soil was that which had been cultivated, even though cover crops had been incorporated. The exact weights, and possibly the relative weights, of the soils would vary considerably with the time of year and condition of the soil at the time the sample was taken. For example, limited tests made just after the cover crop was disced down indicated that at that time the volume weight of the soil under sod was greater than that in the cultivated area.

It is realized that the information given (table 2) is of local application. Nevertheless, it does indicate certain characteristics of the soil which seem of particular value here. It gives us a measure of the looseness, or porosity, of the top soil under the three treatments. It is likely that the lack of organic matter in part accounts for the compactness of the cultivated soil in comparison to that under mulch, but it does not account for the difference between sod and mulch.

This study becomes of more value when the results of the water absorption rates are considered (table 3). Although only 10 determinations were made under each condition, they seem worthy of consideration. These results further indicate the difference in physical character of the soil under the various treat-

TABLE 4

Rates of water absorption by soil (3.1416 sq. in.) per minute

MEANS OF 10 DETERMINATIONS AND STANDARD DEVIATION					
Under mulch		Under sod		Under cultivation	
cc.	*S.D.*	*cc.*	*S.D.*	*cc.*	*S.D.*
1.76	0.79	1.06	0.45	0.58	0.26

	DIFFERENCE BETWEEN TREATMENTS		APPROXIMATE ODDS FOR SIGNIFICANCE OF DIFFERENCE
	cc.	*S.D.*	
Mulch—sod	0.70	0.286	65 to 1
Mulch—cultivation	1.18	0.362	800 to 1
Sod—cultivation	0.48	0.164	270 to 1

ments. As may be noted from table 3, the greatest difference is between the absorption of water under mulch and in the cultivated plot. This is as would be expected from the relative volume weights of the soils (table 2).

These results of water absorption must be considered only from a relative viewpoint. The type of soil, water content, local drainage, and other factors determine the specific results obtained. The relative results strengthen the conclusion drawn from the volume weight tests—that mulch and sod soils are more porous than the cultivated ones.

SUMMARY

This investigation was conducted in order to secure definite measurements of the differences in organic matter content and porosity of an orchard soil which had been under certain cultural systems for a comparatively long time.

In these studies, the organic matter content of a Wooster silt loam under three definite cultural systems, cultivation, sod, and mulch, was determined by the chromic acid method. Under the conditions of these studies, the organic matter content was about the same under the mulch and sod, but it was much lower in the cultivated area, even though a system of cover crops had been used there.

A measurement of the porosity of the soil under sod, mulch, and cultivation was obtained by volume-weights and also by rapidity of water absorption. Such measurements are variable, but relative differences in the results were consistently comparable. In the order of greatest volume-weight and lowest rate of water absorption, they were: cultivation, sod, and mulch.

In each case, the difference between the results under cultivation and sod was greater than the difference between those under sod and mulch.

REFERENCES

(1) ALLISON, L. E. 1935 Organic soil carbon by reduction of chromic acid. *Soil Sci.* 40: 311.

(2) AUTEN, J. T. 1933 Porosity and water absorption of forest soils. *Jour. Agr. Res.* 46: 11: 997.

(3) DEGTJAREFF, W. F. 1930 Determination of soil organic matter by means of hydrogen peroxide and chromic acid. *Soil Sci.* 29: 239.

(4) HAVIS, LEON, AND GOURLEY, J. H. 1936 Some relationships of cultural systems to soil organic matter. *Amer. Soc. Hort. Sci. Proc.* 33: 99.

(5) SCHOLLENBERGER, C. J. 1927 A rapid approximate method for determining soil organic matter. *Soil Sci.* 24: 65.

(6) SCHOLLENBERGER, C. J. 1931 Determination of soil organic matter. *Soil Sci.* 31: 483.

(7) SHAW, J. K., AND SOUTHWICK, L. 1936 Heavy mulching in bearing apple orchards. Mass. Agr. Expt. Sta. Bul. 328.

THE LAWS OF SOIL COLLOIDAL BEHAVIOR: XVIII. COLLOIDAL ELECTROLYTES

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INTRODUCTION

At present much work is devoted to a study of the structure and constitution of soil colloids or of compounds present in soil colloids. The result of this work will probably be the same as the result of the work on humus by Schreiner and Shorey: many valuable discoveries and many compounds identified, but not humus. The reactive material of soil colloids (which always includes humus) cannot possess a definite composition and structure. Its mode of reaction and its products of decomposition, which vary with the pH, prove this.

But in spite of this lack of definiteness in composition, it has been possible to undertake a systematic study of soil colloids on the basis of the acidic and basic material which enters into their make-up. The ratio of the activities of the acidic and basic groups governs the chemical behavior of the soil colloid. It is this relationship which enables us to undertake a systematic study of the chemistry of soil colloids even though we are entirely ignorant of composition and structure. Whether it be a mineral gel of the most indefinite composition, or whether it be the most complex of all terrestial matter, the humus, its most important function as a chemical entity will be an orderly expression of the relative activities of its acidic and basic groups.

It is the object of this paper to show that the reactions of the soil colloidal complex are fundamentally the same as the reactions of weak electrolytes. It will be shown that the isoelectric precipitation, the reactions of the colloids with acids and bases and with neutral salts, and the reactions between the colloids themselves can all be accounted for by a special application of the known laws of ordinary weak acids and bases, and ampholytes.

COLLOIDAL ACIDS, BASES, AND SALTS

The colloidal condition of the soil acidoids and basoids does not prevent them from reacting in the same manner in which ordinary acids and bases react. The difference between colloidal and ordinary electrolytes is primarily a difference in degree, not in kind. Electrolytes exist in all degrees of dispersion, the "true" solution of ordinary electrolytes representing the ultimate state of dispersion.

We cannot, however, apply the mass law to colloidal electrolytes, for we have no way of telling their concentration or reacting masses, either of which if greatly modified by their state of aggregation. Another distinction of colloidal electrolytes is that not only the acidoids and basoids, but also their salts (the saloids), undergo a limited degree of dissociation. Another important distinction is that there is no stoichiometry in the colloidal complex, beyond a balance between positive and negative ions. Any proportion of acidoid and basoid may enter into the make-up of the complex, and the saloid may exist in association with various proportions of its products of hydrolysis, in so far as these remain in the colloidal condition. There is no such thing as a pure colloid. The term is meaningless, for any attempt to purify a colloid changes its identity. We might as well attempt to purify living matter.

The colloidal acids and bases in the soil complex may be very weak, and yet, because of the low dissociation of their salts, may possess a considerable

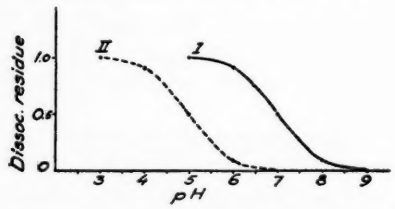


FIG. 41. I. The dissociation residue of an acid whose dissociation constant = 1×10^{-7}. II. The same in the presence of a cation with which the acid forms a slightly dissociated salt

power to combine, mutually, with each other, and with other acids and bases or with their anions and cations. This is illustrated in figure 41 (*a*).

The full-drawn curve in the figure represents the dissociation residue, or uncombined part, of a monobasic acid, whose dissociation constant $K_a = 10^{-7}$, when combining with a base with which it forms a completely dissociated salt. The dissociation residue p is calculated by the equation

$$p = \frac{1}{1 + \frac{K_a}{(H^+)}} \qquad (A)$$

and is about 99 per cent at pH 5, 50 per cent at pH 7, and about 1 per cent at pH 9. (The residue curve is the mirror image of the dissociation curve.)

If, however, the reaction takes place in the presence of a cation I^+ with which the acid anion forms a slightly dissociated salt, then the power of the acid to neutralize base will be increased. The acid will act as if it were a stronger acid, its apparent dissociation constant being greater than its true constant.

For the case in which the cation I^+ is present in sufficient excess, so that its

interaction with the acid does not materially affect its concentration, Michaelis (11) derives the following expression for the dissociation residue

$$p = \frac{1}{1 + \frac{K_a}{(H^+)}\left(\frac{i^+}{K_s} + 1\right)} \qquad (B)$$

where i^+ is the concentration of the cation and K_s the dissociation constant of the salt.

If we assume that $i^+ = 0.1\ N$ and that $K_s = 0.001$, and calculate p at different hydrogen-ion activities, we obtain the broken curve in figure 41 (a). The position of the curve would be the same for $i^+ = 1.0\ N$ and $K_s = 0.01$ or any other set of values whose ratio $\frac{i^+}{K_s} = 100$.

The effect of the presence of the cations will, in the assumed case, be the same as if the dissociation constant of the acid were 10^{-6} instead of 10^{-7} (pK = pH at $p = 0.5$).

The lower the dissociation of the salt which a cation forms with an acid anion, the more successfully do the cations compete with, and displace the H ions of the acid, and the stronger does the acid appear to be. The same is true of a base. We shall later account for the neutral salt reaction on the basis of this principle.

In addition to the above special effect of a salt upon the combining capacity of acids and bases in the case of true salt formation, there is the general effect of a salt upon the activity of the anions and cations of the reacting acid or base. When we determine the hydrogen-ion "concentration," or pH, we measure the activity, and not the concentration, of these ions. The constant K in the "buffer equation," from which equations (A) and (B) are derived, is related to the activity, and not to the concentration, of the ions. It is a true constant only as an activity constant. The "buffer equation" is, therefore, only an approximation unless the anion concentration of the acid is multiplied by the activity factor f_a:

$$(H^+) = \frac{K \times [\text{free acid}]}{f_a \times [\text{anions of the acid}]}.$$

The value of f is smaller the higher the valence of the anions and the greater the salt concentration or, strictly speaking, the ionic strength of the solution. In the case of colloidal acids and bases, we do not know the valence and cannot calculate f, but the value of this factor will reflect itself in the apparent dissociation constant

$$k' = \frac{K}{f}$$

Since $f < 1$, $k' > K$, that is, the activity effect of the addition of a salt will be such as to make it appear as if the dissociation constant had become greater,

exactly as in the above case of true salt formation, where the factor within the parenthesis in formula (*B*) reflects itself in the apparent constant

$$k'' = K\left(\frac{i^+}{K_s} + 1\right)$$

The combined effect of both factors will be expressed by the apparent dissociation constant

$$k = \frac{K\left(\frac{i^+}{K_s} + 1\right)}{f}$$

which, when substituted in the buffer equation, gives the correct relationship, thus

$$(H^+) = k\,\frac{[\text{free acid}]}{[\text{anions of the acid}]}$$

To illustrate the interaction of colloidal acids and bases let us, for the sake of analogy with the soil basoids, begin with a tri-acidic base, $B(OH)_3$, with the apparent dissociation constants $k_{b_1} = 10^{-7}$, $k_{b_2} = 10^{-8}$, and $k_{b_3} = 10^{-9}$. The capacities y_1, y_2, y_3 to bind acid are calculated from the equation

$$y = \frac{c}{1 + \frac{(OH^-)}{k_b}} \qquad (C)$$

where c = concentration of the base. Putting $c = 1$ we get approximately the values given in table 144 (A). By plotting Σy against pH we obtain the curve on the left in figure 42 (*a*). At pH 9 the base binds about 0.01 equivalent of acid, and at pH 3 it has combined with approximately 3.0 equivalents of acid.

Since the base is colloidal it will pass through three forms of aggregation between pH 9 and 3 as follows:

the gel form
the sol form
"true" solution

In the uncombined state the base will exist in the gel condition as $[B(OH)_3]_n$. This is indicated by the full-drawn section of the curve. As the base combines with an acid, i.e., HCl, etc., with which it forms a dissociating salt, it becomes ionized and changes gradually to the sol condition, in which the base exists as $[B(OH)_2^+]_n$, or $(BOH^{++})_n$, or any mixture of these. This is indicated by the broken section of the curve. Finally, the base becomes fully ionized as B^{+++} and passes into "true" solution, as indicated by the dotted section of the curve.

Since the base must be assumed to react amphoterically like the weak

soil bases aluminum and iron hydroxides, it must possess an iso-electric point. If we assume its apparent acid dissociation constants to be $k_{a_1} =$

TABLE 144

(*A*) *Capacity to bind acid when* $k_{b_1} = 10^{-7}$; $k_{b_2} = 10^{-8}$; $k_{b_3} = 10^{-9}$
c = 1.0 mol base

(H^+) (OH^-)	10^{-2} 10^{-12}	10^{-3} 10^{-11}	10^{-4} 10^{-10}	10^{-5} 10^{-9}	10^{-6} 10^{-8}	10^{-7} 10^{-7}	10^{-8} 10^{-6}	10^{-9} 10^{-5}	10^{-10} 10^{-4}
y_1	1.00	1.00	1.00	0.99	0.91	0.50	.09	.01	
y_2	1.00	1.00	0.99	.91	0.50	0.09	.01		
y_3	1.00	.99	.91	.50	.09	.01			
Σy	3.00	2.99	2.90	2.40	1.50	.60	.10	.01	

(*B*) *Capacity to bind base when* $k_{a_1} = 10^{-5}$, $k_{a_2} = 10^{-6}$, $k_{a_3} = 10^{-7}$
c = 0.1 mol acid

x_1		0.001	0.009	.050	.091	.099	.100	.100	.100
x_2			.001	.009	.050	.091	.099	.100	.100
x_3				.001	.009	.050	.091	.099	.100
Σx			.01	.06	.15	.24	.29	.30	.30
$\Sigma x - y$	−3.00	−2.99	−2.89	−2.34	−1.35	−.36	.19	.29	.30

(*C*) c = 0.5 mol acid

x_1		.005	.045	.250	.455	.495	.500	.500	.500
x_2			.005	.045	.250	.455	.495	.500	.500
x_3				.005	.045	.250	.455	.495	.500
Σx		.005	.05	.30	.75	1.20	1.45	1.50	1.50
$\Sigma x - y$	−3.00	−2.98	−2.85	−2.10	−.75	.60	1.35	1.49	1.50

(*D*) c = 1.0 mol acid

x_1		.01	.09	.50	.91	.99	1.00	1.00	1.00
x_2			.01	.09	.50	.91	.99	1.00	1.00
x_3				.01	.09	.50	.91	.99	1.00
Σx		.01	.10	.60	1.50	2.40	2.90	2.99	3.00
$\Sigma x - y$	−3.00	−2.98	−2.80	−1.80	±0.0	1.80	2.80	2.98	3.00

10^{-9}, $k_{a_2} = 10^{-10}$, and $k_{a_3} = 10^{-11}$ and calculate the capacities x_1, x_2, x_3 to bind base from the equation

$$x = \frac{1}{1 + \frac{(H^+)}{k_a}} \qquad (D)$$

we get the right hand curve in figure 42 (*a*) as an expression for Σx. The amphoteric hydroxide would, therefore, be isoelectric at pH 8, for here it combines with equal quantities of acid and base. The described hydroxide would resemble aluminum hydroxide, which has been found to be isoelectric at pH 8.1, when precipitated from the chloride by NaOH.

We shall now consider the interaction of the colloidal hydroxide with varying proportions of a tribasic, colloidal acid, H_3A, with which it forms a slightly dissociated, colloidal salt. We shall assume that the acid, when reacting with

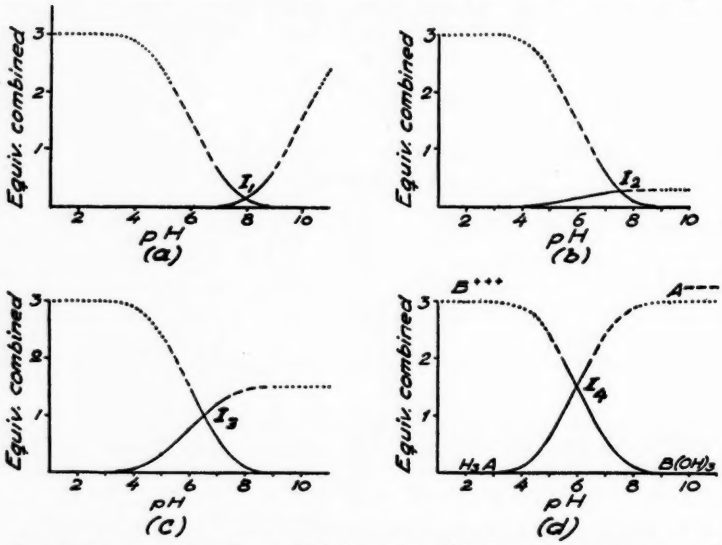


FIG. 42. The capacities to bind acid (left) and base (right) and the isoelectric point I of colloidal systems containing:

(*a*) an amphoteric hydroxide $B(OH)_3$ ($k_{b_1} = 10^{-7}$, $k_{b_2} = 10^{-8}$, $k_{b_3} = 10^{-9}$, and $k_{a_1} = 10^{-9}$, $k_{a_2} = 10^{-10}$, $k_{a_3} = 10^{-11}$)

(*b*), (*c*), and (*d*) 1 mol of the hydroxide $B(OH)_3$ (basic function) and 0.1, 0.5, and 1.0 mol, respectively, of an acid H_3A ($k_{a_1} = 10^{-5}$, $k_{a_2} = 10^{-6}$, $k_{a_3} = 10^{-7}$) k = apparent dissociation constant

the hydroxide, possesses the apparent constants $k_{a_1} = 10^{-5}$, $k_{a_2} = 10^{-6}$, $k_{a_3} = 10^{-7}$.

In order to simplify the relationship we shall consider only the basic function of the hydroxide (y values) and ignore its function as acid (x values), not forgetting, however, that at pH above 8 the hydroxide does function as an acid and binds base.

Table 144 (B), (C), and (D) give the capacities, x_1, x_2, x_3, of 0.1, 0.5, and 1.0, mol of the acid H_3A to bind base, respectively. The Σx values of 0.1, 0.5, and 1.0 mol acid are plotted together with the Σy values of 1.0 mol of the hydroxide in figure 42 (*b*), (*c*), and (*d*), respectively.

The $\Sigma\ x - y$ values in the table show the *net* capacities of the different combinations to bind acid (negative values) and base (positive values) and are represented by the figures by the vertical distance between the two curves: the negative values on the left and the positive values on the right. The pH at which $\Sigma\ x - y = 0$ corresponds to the point of intersection of the curves and represents the isoelectric point of the complex.

We note that the addition of increasing amounts of the acid H_3A to a given amount of the hydroxide leads to:

A decrease in the power to bind acid and to exchange anions, within a certain range of reaction, in which the added acid has tied up a certain amount of the hydroxide, thus leaving a smaller basic residue

An increase in the power to bind base and to exchange cations, due to an increment in the acidic residue of the complex

A deflection of the isoelectric point to the acid side and, consequently, a stabilization of the complex in the same direction

To illustrate the effect of a further addition of acid, figure 43 (*a*) is presented, which shows the position and intersection of the curves up to 8 mols of H_3A to 1 mol $B(OH)_3$. From the position of the curves, it is evident that the deflection of the isoelectric point becomes smaller, gradually approaching a limit as we increase the amount of acid.

This relationship is brought out more clearly by plotting the molar ratio $H_3A/B(OH)_3$ against the isoelectric pH (the points of intersection in figure 43 (*a*) as in figure 44 (*a*), curve I). Note how closely this curve agrees, with respect to position and form, with the experimental curve in figure 44 (*b*), obtained by isoelectrically precipitating humic acid and aluminum hydroxide and adapted from figure 10 in this series (4).

It should also be noted that the deflection of the isoelectric point is related not only to the molar ratio of acid to hydroxide but to their apparent dissociation constants as well. This, again, is best illustrated graphically. If instead of the acid H_3A, we add to the hydroxide the acid H_3A', whose apparent dissociation constants are $k'_{a_1} = 10^{-7}$, $k'_{a_2} = 10^{-8}$, and $k'_{a_3} = 10^{-9}$, and plot the corresponding curves, we obtain the results shown in figures 43 (*b*) and 44 (*a*), curve II. It will be seen that the weaker acid H_3A' gives, with the hydroxide $B(OH)_3$, an isoelectric series, which covers a smaller range of pH than the series formed with the stronger acid; that is, the weaker acid deflects the isoelectric point less, and attains the limiting value more abruptly than the stronger acid. By extrapolation we see that a sufficiently weak acid would not combine with the hydroxide and would not affect its isoelectric point. A stronger acid would produce the opposite effect, giving a greater deflection and, therefore, a wider isoelectric series. The effect of the strength of the hydroxide in combination with a given acid would be the same, a stronger hydroxide giving a wider isoelectric series than a weaker one.

With reference to the effect of acids of different strength on the net capacity of the complex to bind base and to exchange cations, an inspection of figure

43 (*a*) and (*b*) will show that, at a given pH, not too far above the isoelectric points, e.g., at pH 7, the stronger acid produces the greatest effect: *The lower the isoelectric point the greater is the cation exchange capacity.* At very high pH, however, this difference vanishes, for even the weakest acid will bind as

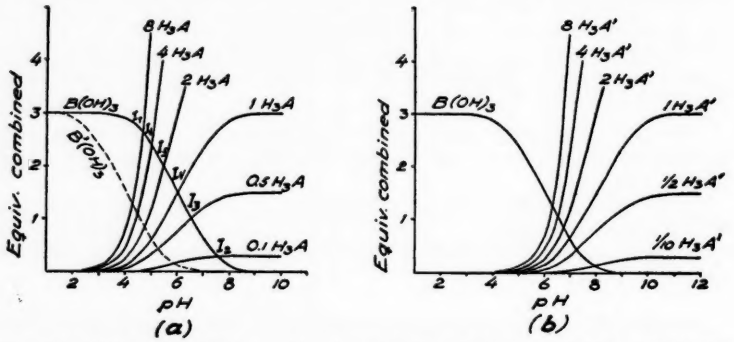


FIG. 43. (*a*) 1 mol $B(OH)_3$ in combination with 0.1 to 8 mols H_3A (cf. fig. 42) $B'(OH)_3$ represents a weaker hydroxide

(*b*) 1 mol $B(OH)_3$ in combination with 0.1 to 8 mols of a weaker acid H_3A' ($k_{a_1} = 10^{-7}$, $k_{a_2} = 10^{-8}$, $k_{a_3} = 10^{-9}$.

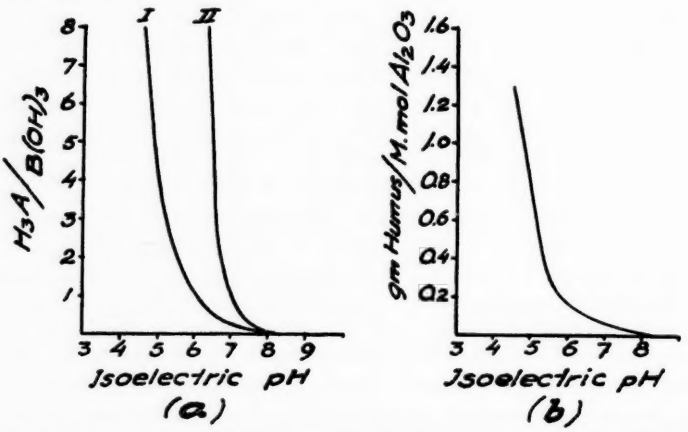


FIG. 44. (*a*) The relationship between the ratio $H_3A/B(OH)_3$ and the isoelectric point. Curve I is based on fig. 43 (*a*) and curve II, on fig. 43 (*b*)

(*b*) The corresponding relationship in an isoelectrically precipitated Al-humate series

much base as the strongest at sufficiently high pH. Hence, laterites bind as much, or more, base than silicious colloids at high pH value.

The effect of the strength of the hydroxide on the cation exchange will be the opposite to that of the acid. To illustrate this, let us consider the interaction of the acid H_3A with a weaker hydroxide $B'(OH)_3$, having the apparent

dissociation constants $k'_{b_1} = 10^{-9}$, $k'_{b_2} = 10^{-10}$, and $k'_{b_3} = 10^{-11}$. Its capacity to bind acid ($\Sigma\, y'$) is represented by the broken curve in figure 43 (*a*). An inspection of the figure shows that the isoelectric points are lower in all cases, and that the acidic residues, and, therefore, the power to bind base and exchange cations, are greater. This agrees with the observed facts that the ferric complexes (silicates, humates, and phosphates) have a lower isoelectric point and a greater cation exchange capacity than the aluminum complexes of corresponding composition (5).

We shall now complete the graphic presentation by plotting the $\Sigma\, x-y$ values of 1 mol of the hydroxide $B(OH)_3$ in combination with various proportions (0.1 to 8 mols) of the acid H_3A against the pH. Figure 45 (*a*) shows the central portions of the titration or buffer curves thus obtained, which represent the net capacities of the different systems to bind acid (negative values) and base (positive values). The point at which a curve intersects the line corresponding to the zero position on the abscissa is the isoelectric point of the complex. Similar series of curves have been obtained by titrating isoelectrically precipitated silicates, phosphates, and humates of aluminum and iron (10).

For comparison with figure 45 (*a*), figure 45 (*b*), (*c*), and (*d*) are here reproduced. Figure 45 (*b*) shows the titration curves of two isoelectrically precipitated and electrodialyzed alumino silicates together with aluminum hydroxide; (*d*) shows the titration curves of a corresponding series of phosphates; whereas (*c*) shows the titration curves of three electrodialyzed soils, namely, the Nipe laterite, the Sassafras loam, and the Sharkey clay soil. The figures on the soil curves give the SiO_2/M_2O_3 ratios in the soil colloids. The slope of the curves depends, of course, upon the concentration of the colloid and upon the scale chosen. But the point of intersection with the zero line is determined, apart from the dilution effect, by the isoelectric point of the complex. It will be noted that this point is lower, the higher the acidoid/basoid ratio, exactly as in the theoretical case.

In studying the amphoteric humates of aluminum and iron an anomaly was encountered. It was found that the humate systems, having a high proportion of humic acid and, therefore, a low isoelectric point, possess a second isoelectric point at a still lower pH, and that systems having a very high proportion of humic acid remain anodic, having no isoelectric point, no matter how low the pH (4). There is no theoretical basis for this behavior in figure 43. The functions x and y express the sum of true salt formation and dissociation, and the isoelectric point is defined as the point where the anionic and cationic dissociation of the complex are equal, or where $\Sigma\, x-y = 0$. But dissociation is not alone responsible for the potential difference at the interface, and the charge of the colloid. The charge may also be caused by an association with ions, and by an interaction with electrical dipoles. The fact is that inert substances in general charge themselves negatively in water. This being the case, we must assume that all colloids dispersed in water possess

a residue e of negative charge apart from their ionization. An amphoteric colloid cannot, therefore, be isoelectric before the dissociation of anions exceeds the dissociation of cations by an amount equal to e. In other words, the isoelectric point will be at the pH where $y = x + e$, and not where $y = x$.

This alone would not explain the second isoelectric point at a lower pH and the return of the complex to the anionic or negative condition, because a lowering of the pH will result in a greater ionization of the basic group, and a repression of the ionization of the acidic group; i.e., in an increase in y and a decrease in x. The value of y should sooner or later be equal to $x + e$, pro-

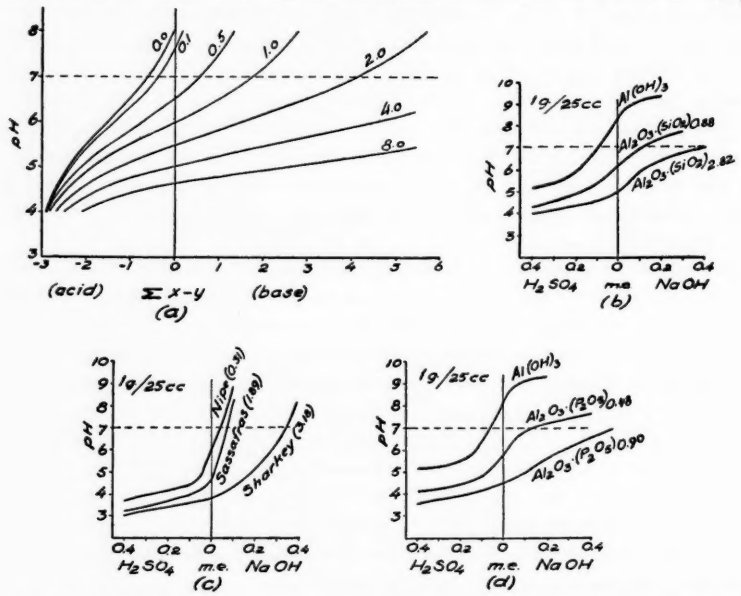


FIG. 45. (*a*) The titration curves of systems containing 1 mol $B(OH)_3$, and 0.0 to 8 mols H_3A (cf. fig. 43 (*a*))

(*b*), (*c*), and (*d*) The titration curves of isoelectrically precipitated aluminum hydroxide, silicates and phosphates, and of 3 soils

vided the proportion of basoid is large enough to make $y > e$. But since the pH is lowered by an acid (HCl) with which aluminum hydroxide forms a soluble salt, Al ions pass into solution, whereas the colloidal humic acid remains in the complex. The positive charge of the latter is thereby reduced until we get a second isoelectric point and finally, when e dominates, an anionic complex. There must be a certain minimum of basic groups in the complex in order to render it electropositive or isoelectric, and since this minimum cannot be maintained at low pH, because of the solubility of the hydroxide, a complex with a high proportion of acidoid must remain anionic. This does

not, however, prevent such a complex from reacting amphoterically: Soil colloids which have a high acidoid/basoid ratio have no isoelectric point but react amphoterically, combining with anions as well as with cations. They are characterized by an equi-ionic point (9). This is defined as the pH at which the anions and cations of a salt are equally adsorbed by the complex, and at which the salt produces neither exchange alkalinity nor exchange acidity. The equi-ionic point is determined by the capacity of the whole system to bind acid and base, whereas the isoelectric point is determined by a balance of the positive and negative charges remaining attached to the complex.

PRECIPITATES OF SOLUBLE ACIDS AND COLLOIDAL HYDROXIDES

In the foregoing we have assumed that the interacting acid and hydrous oxide are themselves colloidal. It is then obvious that both components, no matter in what proportions they are added to the system, will, quantitatively, be precipitated in the isoelectric complex. Aluminum hydroxide and humic acid form such a system. In the experimental work referred to, the humic acid was completely precipitated at the isoelectric points. The experimental curve, relating the composition ratio to the isoelectric pH, shown in figure 44 (*b*), resembles, therefore, the theoretical curves in figure 44 (*a*), which express the total number of mols of H_3A per mol $B(OH)_3$, whether combined or uncombined.

But if the acid is soluble, it will be only the combined fraction which will be precipitated. The remainder will remain in solution. If the acid H_3A were a soluble acid, a part of it would remain in solution even at the isoelectric point where the union between the acid and the hydroxide is a maximum (cf. fig. 43 (*a*)). Table 145 (A) gives the approximate combined and uncombined mol fractions of H_3A at the isoelectric points of the different mixtures, as based on figure 43 (*a*). We note that the uncombined fraction increases rapidly as the amount of added acid is increased and as the isoelectric pH is decreased, and, conversely, that the combined fraction is proportionally much greater in low, than in high, concentrations of the acid. The relationship is shown graphically in figure 46 (*a*), curve I. The scattered figures along the curve represent the isoelectric points. Curve II is based on figure 43 (*b*). We thus obtain an "adsorption" isotherm on a purely chemical basis.

Figure 47 (*a*) shows the total number of mols H_3A per mol $B(OH)_3$ in the mixture and the combined number of mols H_3A, each in relation to the isoelectric pH. If now the acid is soluble, and the uncombined fraction remains in solution, we would get isoelectric precipitates, whose composition is expressed by the lower curve, and not by the upper curve, which expresses the composition of the mixture. It will be noted that the lower curve runs asymptotic to a certain composition, in this case to $H_3A/B(OH)_3 = 1$, whereas the upper curve runs asymptotic to a certain pH. This means that the composition ratio, acid/hydroxide, in the precipitate is in one case (when the acid is soluble) limited and in the other case (acid colloidal) unlimited.

We shall now see that the theory here developed is in perfect agreement with the experimental results obtained in the isoelectric precipitation of systems containing soluble acids and colloidal hydroxides, such as the phosphates and silicates of aluminum and iron. Silicic acid behaves in the dilutions employed, and when freshly prepared, as a soluble acid.

TABLE 145

A graphic presentation is given in fig. 46(*a*) and (*b*) and fig. 47(*a*) and (*b*)

(*A*) *The combined and uncombined mol fractions of* H_3A ($k_{a_1} = 10^{-5}$, $k_{a_2} = 10^{-6}$, $k_{a_3} = 10^{-7}$ *at the isoelectric points when mixed, in the given proportions, with* $B(OH)_3$ ($k_{b_1} = 10^{-7}$, $k_{b_2} = 10^{-8}$, $k_b^3 = 10^{-9}$) *as based on fig. 43(a)*

MOLS $B(OH)_3$ IN MIXTURE	MOLS H_3A IN MIXTURE	ISOELECTR. pH (APPROX.)	MOLS H_3A COMBINED (APPROX.)	MOLS H_3A UNCOMB. (APPROX.)
1	0.1	7.55	0.09	0.01
1	0.5	6.55	0.33	0.17
1	1	6.0	0.50	0.50
1	2	5.45	0.67	1.33
1	4	5.0	0.80	3.20
1	8	4.6	0.88	7.12

(*B*) *The corresponding figures obtained by the isoelectric precipitation of different alumino phosphates**

MOLS $AlCl_3$ IN MIXTURE	MOLS Na_2HPO_4 IN MIXTURE	ISOELECTR. pH	MOLS PO_4 IN PRECIPITATE	MOLS PO_4 IN SOLUTION	COMPOSITION OF PRECIPITATE
5.00	2.495	6.45	2.410	0.085	$Al_2O_3 \cdot (P_2O_5)_{0.48}$
5.00	5.482	5.6	3.843	1.639	$Al_2O_3 \cdot (P_2O_5)_{0.77}$
4.96	10.156	4.9	4.252	5.904	$Al_2O_3 \cdot (P_2O_5)_{0.86}$

(*C*) *The corresponding figures obtained by the isoelectric precipitation of different alumino silicates**

MOLS $AlCl_3$ IN MIXTURE	MOLS Na_2SiO_3 IN MIXTURE	ISOELECTR. pH	MOLS SiO_2 IN PRECIPITATE	MOLS SiO_2 IN SOLUTION	COMPOSITION OF PRECIPITATE
5.00	3.562	6.6	2.734	0.828	$Al_2O_3 \cdot (SiO_2)_{1.09}$
5.00	6.713	6.25	4.072	2.641	$Al_2O_3 \cdot (SiO_2)_{1.63}$
5.00	16.650	4.7	6.443	10.207	$Al_2O_3 \cdot (SiO_2)_{2.62}$
7.50	37.500	4.2	10.660	26.840	$Al_2O_3 \cdot (SiO_2)_{2.90}$

* The phosphate and silicate mixtures in total volumes of 2500 cc.

Table 145 (B) and (C) gives the composition of the mixtures (first and second columns), the isoelectric pH, the quantities of acid in the precipitate and in the solution after precipitation, and the composition of the isoelectric precipitates of the aluminum phosphate and silicate systems.

For a better comparison with the above described theoretical case, the results have been plotted in a similar way in figures 46 (*b*) and 47 (*b*). We note in figure 46 (*b*) that the hydroxide precipitates almost completely small

amounts of silicic acid and, especially, phosphoric acid, but that the higher isoelectric phosphates and silicates exist in equilibrium with ever-increasing quantities of phosphoric and silicic acid in solution. The isoelectric composition in relation to the pH is shown in figure 47 (*b*). The composition of the precipitate does not follow the composition of the mixture as in the case of the humates (acid colloidal), but approaches a limiting value which, for the phosphates, appears to be $PO_4/Al = 1$ and, for the silicates, $SiO_3/Al = 1.5$.

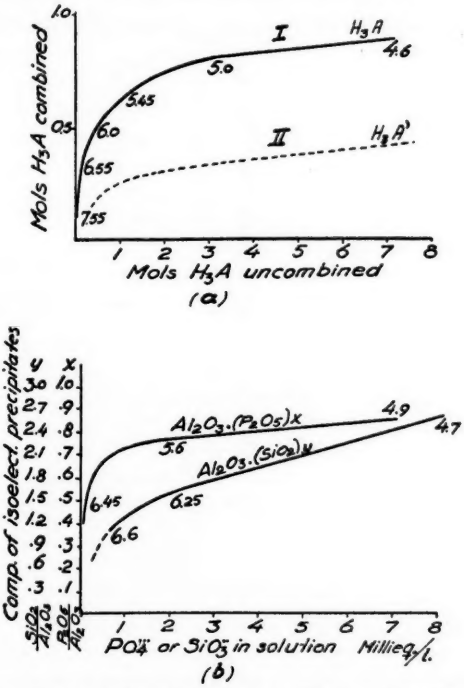


FIG. 46. (*a*) Curve I. The relationship between the H_3A combined with $B(OH)_3$ and that uncombined, as based on fig. 43 (*a*) (cf. table 145 A). Scattered figures represent isoelectric points. Curve II is based on fig. 43 (*b*)

(*b*) The relationship between the combined and uncombined H_3PO_4 and H_2SiO_3 in various isoelectric alumino phosphate and silicate systems (cf. table 145 (B) and (C))

The fact that the isoelectric phosphates and silicates, especially the higher ones, exist in equilibrium with a certain amount of free acid in solution is of interest in relation to soil formation. It means that these and similar compounds are unstable even at their isoelectric point, at which their stability is at a maximum. For if the free acid is removed by leaching or otherwise, a new equilibrium must be established. The acid lost by the solution will be replaced partially at the expense of the complex, whose isoelectric point is

thereby deflected to a higher pH. The process is best illustrated by stating that the composition and the isoelectric point will move from left to right in figure 43.

Another result of the solubility of the acid is that, when the basic constituent becomes ionized and soluble at pH below the isoelectric point, the whole complex will dissolve and vanish as a colloidal entity. In this case a complex will not be formed (as in the case where the acid is colloidal) which is richer in acid and poorer in hydroxide, and which has a lower isoelectric point, than the original complex. In other words, the composition and the isoelectric

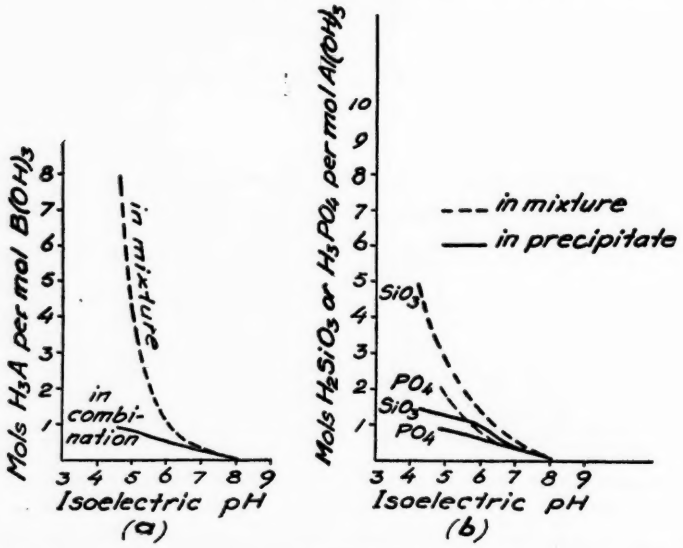


FIG. 47. (*a*) The relationship between the ratio $H_3A/B(OH)_3$ in the mixture and in combination, and the isoelectric point as based on fig. 43 (*a*) (cf. table 145 (A))

(*b*) The corresponding relationship in the isoelectric alumino phosphate and silicate systems (cf. table 145 (B) and (C))

point cannot, in this type of colloid, move from right to left in figure 43 by a mere leaching out of the ionized basic group, because the unionized but soluble acid will simultaneously be lost.

As far as the phosphates are concerned we have, of course, complete solubility of the acid constituent. But phosphoric acid represents such a small percentage of the soil that its practically complete retention is, according to figure 46 (*b*), assured. It should be pointed out that the relatively large mol fraction of phosphoric and silicic acid which, according to table 145, remained in solution, becomes very much smaller in the soil, where the ratio of solution to the solid phase is several thousand times smaller than in the experiments.

Regarding the silicates, it must be remembered that the isoelectric precipitates were prepared in very dilute solutions by adding Na_2SiO_3 to $AlCl_3$. If, instead of the sodium salt, a silicic acid sol was used in the ratio of 14 mols SiO_2 to 1 mol Al_2O_3, a precipitate with the composition $Al_2O_3 \cdot (SiO_2)_{10.35}$ was formed (3). This precipitate had, like the higher humates, no isoelectric point, being anionic over the entire range of precipitation. Large amounts of free silicic acid were obviously precipitated here.

Silicic acid evidently occupies an intermediate position between a soluble and a colloidal acid. When freshly prepared in dilute solution it possesses a high diffusion coefficient, but it quickly ages into a colloidal solution whose stability is affected by several factors. Unlike other negative sols it is sensitized by hydroxyl, or possibly by silicate ions (1). The sol is thus not coagulated by rather large concentrations of neutral salts, whereas small concentrations of the salt will suffice if a little alkali is added. The sol may also be coagulated by the addition of a fine powder, as already observed by Graham (2).

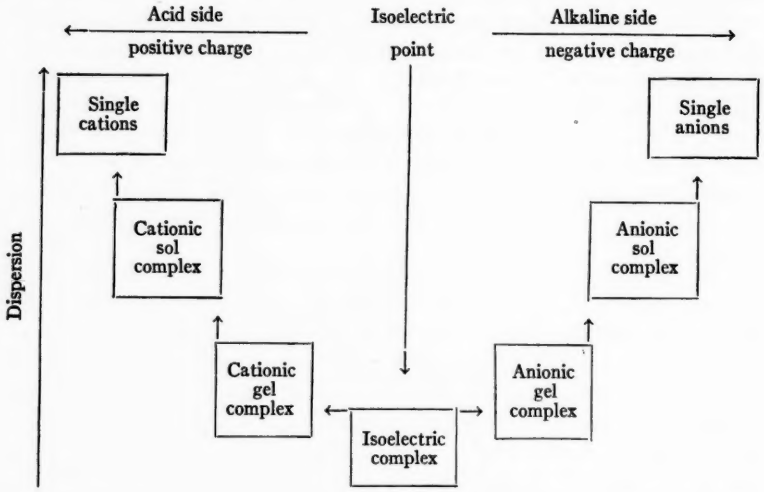
We know very little about how silicic acid interacts in the soil. It seems probable that, unionized, it exists and moves mainly in the colloidal condition. This belief is supported by several facts. Thus, if the basic group of the soil complex is ionized and dissolved by the addition of an acid, much less silica is dissolved than is set free by the decomposition of the silicate. The cation complex is associated with some silica, as it is with humic acid, but this is evidently the result of an incomplete hydrolysis. Similarly, in the A_2 horizon of the podzol profile, after the ionization and leaching of Al and Fe, a complex is left behind which is richer in silica and has a lower isoelectric point than the original material. The process is apparently dominated by the isoelectric type of weathering. If unionized silica were soluble to any appreciable extent, podzolic weathering would lead to a complete solution, and the older soils in humid regions would long ago have lost their silica, and would today be highly lateritic. Isoelectric weathering is, obviously, only then fully realized when the acidic, as well as the basic, constituent of the complex is itself colloidal in the unionized and uncombined condition.

In the foregoing we have discussed the theory of the interaction of colloidal hydroxides with soluble acids. The alternative case, i.e., the interaction of colloidal acids with soluble bases, need not be considered, because all the basic hydrous oxides of the soil are insoluble. The interaction of soluble acids and bases leads to stoichiometric compounds. These play no important rôle in relation to the amphoteric behavior of the soil colloidal complex, beyond the exchange reactions their ions enter into with the latter.

THE ANIONIC AND CATIONIC SOL AND GEL COMPLEX

We shall now introduce a new conception, which, in our opinion, will be not only useful but absolutely essential for an understanding of the intricate processes of soil formation. We have already distinguished between three

states of aggregation: the gel state, the sol state, and the state of ultimate solution of single ions. But, in the case of amphoteric colloids, the series repeats itself on either side of the isoelectric point, with the difference that one series is electronegative, or anionic, and the other is electropositive, or cationic. The material making up the soil colloidal complex may, therefore, exist in seven distinct forms according to the following scheme:



Between these forms we meet with every degree of transition. At the isoelectric point the positive and negative charges are balanced. We do not believe that the charges are equal to zero at this point, because many facts point to a "zwitterionic" condition of the soil complex (8). As the pH of the medium is lowered or raised the gel complex becomes increasingly cationic or anionic, respectively, and passes, at a certain degree of charge, into the sol condition. But the complex not only becomes more highly dispersed; it also undergoes a hydrolytic decomposition.

Let us illustrate this by referring to table 144 (D) and to figure 42 (*d*). Here we have equivalent quantities of H_3A and $B(OH)_3$. At the point I (pH 6) the union between A and B is a maximum, (in this case 50 per cent). This is the isoelectric point. Suppose now that the pH is lowered to about 4.55 by the addition of a strong acid, with which the hydroxide forms an ionized and soluble compound. The hydroxide is here about 90 per cent combined, whereas the acid H_3A is about 90 per cent uncombined, being combined with the hydroxide to the extent of only 10 per cent. The cationic sol complex, which, because of the strong positive charge and the resulting high degree of hydration, splits off from the gel complex, is, therefore, richer in B and poorer in A than the original complex, isoelectric at pH 6. The

liberated acid, H_3A, will, if soluble, pass into solution or it will, if insoluble, remain in the gel, which thereby becomes enriched in this constituent, resulting in a lowering of its isoelectric point (isoelectric weathering). The cationic sol complex will have a higher isoelectric point than the original complex, and this point will be higher the lower the pH at which it was ionized and split off from the gel complex, because the lower the pH the more complete will be the hydrolysis of the complex. At sufficiently low pH the cationic sol complex will resolve itself into single B^{+++} ions.

It must be pointed out that the above holds only for the case in which the acid, which is added to lower the pH of the system, is an acid which forms an ionized compound with $B(OH)_3$. If an acid is added which resembles the acid H_3A in so far that it forms a practically unionized and insoluble compound with $B(OH)_3$, then it is obvious that the complex will not become cationic, and will not disperse, even though the pH be lowered. The effect would then be the same as when the proportion of H_3A is increased, as illustrated in figure 43 (*a*). The isoelectric point would be lowered, and it would, therefore, require a still lower pH to ionize the basic group of the complex. This explains the lowering of the isoelectric point of a soil by the addition of H_3PO_4, or even H_2SO_4, as compared to HCl (6). For this reason an amphoteric colloid is not necessarily isoelectric at the pH where it combines with an equal number of anions and cations, i.e., where $x-y = 0$. This point is better defined as the equi-ionic point.

The effect of an increase in pH will be the opposite, for then it will be the acidic group which will be ionized, forming an anionic sol complex, which is richer in A and poorer in B than the original complex, whereas the latter becomes correspondingly richer in B. (Since $B(OH)_3$ itself is amphoteric it will, of course, ionize and disperse at sufficiently high pH.)

We now come to one of the most important principles of soil formation, namely, the mutual interactions of the soil complexes. To illustrate this, let us assume that the cationic sol complex, which is split off from the parent gel complex at pH 4.55, has the composition of 0.1 mol H_3A to 1 mol $B(OH)_3$. The isoelectric point would, according to figure 43 (*a*), be at pH 7.55. The complex would act as a base and bind acid up to this pH as indicated by the negative $\Sigma\, x-y$ values in table 144 (B). If the pH is increased to 7.55, the cationic sol complex, which we shall designate by the formula $H\cdot a\cdot b^{+}$, would become isoelectric as follows:

$$\underset{\text{cationic sol complex}}{H\cdot a\cdot b^{+}} + OH^{-} \rightarrow \underset{\text{isoelectric gel complex}}{H\cdot a\cdot b\cdot OH} \qquad \text{(A)}$$

But suppose that, during the upward climb of the pH, the cationic sol complex encounters a complex which has a lower isoelectric point such as, for example, the original parent gel complex isoelectric at pH 6. This complex

becomes anionic at a pH above 6, where it begins to act as an acid and to bind base, as indicated by the positive $\Sigma x - y$ values in table 144 (D). Within the range of pH from 6 to 7.55, one complex will act as acid, and the other will act as base. The obvious result of this is a chemical interaction resulting in a new complex, whose isoelectric point will be determined by the proportions of the interacting complexes, but which must be somewhere between pH 6.0 and 7.55. If we designate the anionic gel complex by the formula $^{-}A \cdot B \cdot OH$, we can express the interaction by the following equation:

$$\begin{array}{cccccc} H \cdot a \cdot b^{+} & + & {}^{-}A \cdot B \cdot OH & \rightarrow & H \cdot a \cdot b \cdot A \cdot B \cdot OH & \\ \text{cationic} & & \text{anionic} & & \text{isoelectric} & \text{(B)} \\ \text{sol complex} & & \text{gel complex} & & \text{gel complex} & \end{array}$$

The important difference between the two equations is that in equation (A) the cationic sol complex is precipitated at its own isoelectric point by combining with OH ions, whereas in equation (B) it is isoelectrically precipitated at a lower pH by uniting with an anionic complex. That such mutual interactions between soil colloids actually occur was shown in a previous paper (8). Since this work was published elsewhere a brief resumé will be given in this series.

THE MUTUAL INTERACTIONS OF AMPHOTERIC COLLOIDS

Theoretical. We shall first consider the theoretical aspect of the interaction by constructing the titration curves of two amphoteric colloids (ampholytoids), whose (apparent) $k_a \cdot k_b = 10^{-16}$, but whose isoelectric point is in one case at pH 6 and in the other at pH 3, representing both extremes in soil types.

Assuming the apparent dissociation constants $k_{a_1} = 10^{-7}$ and $k_{b_1} = 10^{-9}$ in the one case, and $k_{a_2} = 10^{-4}$ and $k_{b_2} = 10^{-12}$ in the other case, and putting $c = 1$ in the above formulas (*C*) and (*D*), we obtain the capacities of the ampholytoids to neutralize base (x values) and acid (y values) at different $[H^+]$ as given in table 146.

By plotting the $x - y$ values against $[H^+]$ we obtain the dotted curves in figure 48 (*a*). The isoelectric point I corresponds to the $[H^+]$ at which $x - y = 0$ and may be calculated from the equation (Michaelis).

$$I = \sqrt{\frac{K_a}{K_b} K_w}$$

$$I_1 = \sqrt{\frac{10^{-7}}{10^{-9}} \cdot 10^{-14}} = \sqrt{10^{12}} = \text{pH } 6.0$$

$$\text{and} \quad I_2 = \sqrt{\frac{10^{-4}}{10^{-12}} \cdot 10^{-14}} = \sqrt{10^{-6}} = \text{pH } 3.0 \qquad (E)$$

These curves differ from the experimental curves obtained from a laterite on the one hand, and a humus soil or a silicious clay on the other, in that

the last two do not show an endpoint, i.e., a saturation point, by terminating parallel to the ordinate axis, but continue to bind acid and base over a very wide range of pH. This is, of course, due to the fact that the soil contains a whole series of acidic and basic residues, whose dissociation constants cover,

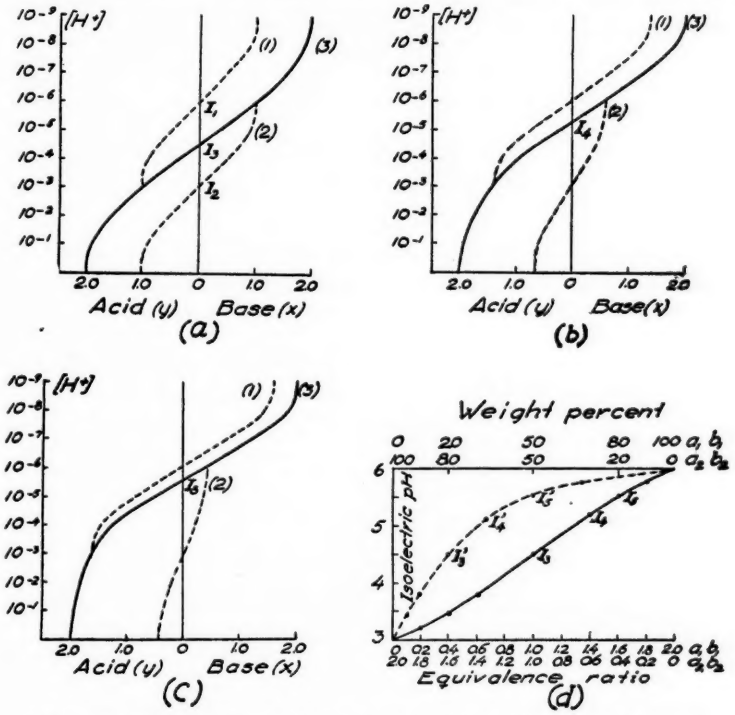


FIG. 48. (*a*) The dotted curves show the net capacities to bind acid and base ($x - y$) of 2 ampholytes isoelectric (1) at pH 6.0 ($K_{a_1} = 10^{-7}$, $K_{b_1} = 10^{-9}$) and (2) at pH 3.0 ($K_{a_2} = 10^{-4}$, $K_{b_2} = 10^{-12}$). The full-drawn curve (3) shows the net capacity of a mixture of a mol of each of the 2 ampholytes ($\Sigma x - y$) (cf. table 146)

(*b*) and (*c*) The capacities of (*b*) a mixture of 1.4 mol of ampholyte (1) and 0.6 mol of ampholyte (2); (*c*) a mixture of 1.6 mols of ampholyte (1) and 0.4 mol of ampholyte (2) (cf. fig. 48 (*a*))

(*d*) The relationship between the isoelectric pH and the equivalence ratio in mixtures of amphoteric colloids, as based on the theoretical curves in fig. 48 (*a*), (*b*), and (*c*). The dotted curve is based on a mass ratio assuming 20 per cent of ampholyte (1) equivalent to 80 per cent of ampholyte (2)

within certain limits, every order of magnitude. The titration curves of soils are compound curves consisting of a whole series of overlapping curves. They represent an amphoteric complex of indefinite composition, and not a definite compound or "soil acid."

By plotting the $\Sigma\, x-y$ values in table 146 against $[H^+]$, we get the titration curve of a system containing one equivalent of each of the two ampholytoids, a_1b_1 and a_2b_2 (cf. the fulldrawn curve in fig. 48 (*a*). We note that the curve is that of an ampholytoid *isoelectric at a pH midway between the isoelectric points of the individual components* or, since this point is governed (in this case) by the strongest acidic and basic groups, at

$$I_3 = \sqrt{\frac{10^{-4}}{10^{-9}} \cdot 10^{-14}} = \sqrt{10^{-9}} = \text{pH } 4.5$$

The ampholytoids interact between pH 3.0 and 6.0. The mutual "neutralization" attains a maximum at pH 4.5, where it amounts to slightly more

TABLE 146

Theoretical capacity to bind base (*x*) *when* $k_{a_1} = 1 \times 10^{-7}$; $k_{a_2} = 1 \times 10^{-4}$

$[H^+]N$ / $[OH^-]N$	10^{-0} / 10^{-14}	10^{-1} / 10^{-13}	10^{-2} / 10^{-12}	10^{-3} / 10^{-11}	10^{-4} / 10^{-10}	10^{-5} / 10^{-9}	10^{-6} / 10^{-8}	10^{-7} / 10^{-7}	10^{-8} / 10^{-6}	10^{-9} / 10^{-5}	10^{-10} / 10^{-4}
x_1						0.01	0.09	0.50	0.91	0.99	1.00
x_2			0.01	0.09	0.50	0.91	0.99	1.00	1.00	1.00	1.00
Σx			0.01	0.09	0.50	0.92	1.08	1.50	1.91	1.99	2.00

Capacity to bind acid (*y*) *when* $k_{b_1} = 1 \times 10^{-9}$; $k_{b_2} = 1 \times 10^{-12}$

y_1	1.00	1.00	1.00	0.99	0.91	0.50	0.09	0.01			
y_2	0.99	0.91	0.50	0.09	0.01						
Σy	1.99	1.91	1.50	1.08	0.92	0.50	0.09	0.01			
$x_1 - y_1$	−1.00	−1.00	−1.00	−0.99	−0.91	−0.49	*0.00*	0.49	0.91	0.99	1.00
$x_2 - y_2$	−0.99	−0.91	−0.49	*0.00*	0.49	0.91	0.99	1.00	1.00	1.00	1.00
$\Sigma x - y$	−1.99	−1.91	−1.49	−0.99	−0.42	0.42	0.99	1.49	1.91	1.99	2.00

than 0.7 equivalence. The salt is completely hydrolyzed below pH 3.0 and above pH 6.0, so that the ultimate capacity of the system to bind strong acids and bases remains the same as that of the individual ampholytoids.

The curves in figure 48 (*a*) represent the case in which the reacting materials are present in equivalent quantities. It is only in such cases that formula (*E*) applies, and that the isoelectric point of the compound ampholytoid lies midway between the points of the single ampholytoids. But two or more ampholytoids may react in any proportion, and the isoelectric point of the mixture may occupy any position between the isoelectric points of the individual components. The relationship between the proportion of the individual ampholytoids and the position of the isoelectric point of the mixture is shown in two cases in fig. 48 (*b*) and (*c*). If a total of two equivalents of ampholytoids, a_1b_1 and a_2b_2, are mixed in the proportions 1.4:0.6 and 1.6:0.4, we get the deflection of the isoelectric point as shown by the position of the

titration curve of each mixture (cf. full drawn curves in fig. 48 (*b*) and (*c*), obtained by plotting Σx-y against $[H^+]$ as in fig. 48 *a*). In this case, the ampholytoid having the lowest isoelectric point is progressively decreased in relation to the ampholytoid having the highest isoelectric point, which is progressively increased. The isoelectric points of the mixtures are, therefore, deflected in the direction of higher pH. If the case were reversed, then the isoelectric points would be deflected from the midway point to lower pH.

By plotting the equivalence ratios of the two ampholytoids against the isoelectric pH, we obtain the full-drawn curve in fig. 48 (*d*). The curve is obtained by a graphic transfer of the corresponding points in figure 48 (*a*), (*b*), and (*c*). It will be noted that the curve is slightly S-shaped. This happens whenever the slopes of the titration curves depart from uniformity before they leave that range of pH which lies between the isoelectric points of the individual ampholytoids, in our case, between pH 3 and 6. When the titration curves are uniform within this range, that is, when the power of the individual ampholytoids to bind acid and base is a linear function of the pH, the curve in figure 48 (*d*) will become a straight line. In the case of soils, which represent compound ampholytoids, and which, therefore, bind acids and bases over a wide range of pH, the above condition is often fulfilled, although irregularities in their titration curves are not uncommon.

The most significant point on the curve in figure 48 (*d*) is the point I_3 midway between the isoelectric points of the individual ampholytoids. A mixture isoelectric at this point must contain the ampholytoids in equivalent proportions. Suppose that the two ampholytoids yield an isoelectric mixture at pH 4.5 when taken in the proportion of 0.4 part by *weight* of a_1b_1 and 1.6 parts of a_2b_2 (20 per cent and 80 per cent). We know then that these proportions contain an equal number of chemical equivalents, and that the ratio of the equivalent weight of a_1b_1 (as base) to a_2b_2 (as acid) is as 0.4:1.6. If we now, on the basis of this assumption, plot the isoelectric pH against the percentage ratio in place of the equivalence ratio, we get the dotted curve in figure 48 (*d*) (obtained by multiplying the a_1b_1 equivalents on the abscissa by 20 and the a_2b_2 equivalents by 80, and transposing the corresponding points to the new ratio, I_3 to I_3', I_4 to I_4', etc.). If we assume a lower equivalent weight for ampholytoid a_2b_2 than for ampholytoid a_1b_1, then it will require a smaller amount (by weight) of the former than of the latter to yield an isoelectric mixture at a point midway between the isoelectric points of the individual ampholytoids. This point will then lie on the right side of I_3 in figure 48 (*d*) and we shall obtain a curve concave to the ordinate axis.

We shall now see that mixtures of soils having different equi-ionic points[1] yield the type of curves the theory demands.

[1] The pH of exchange neutrality, i.e., the pH at which a soil binds equivalent quantities of anions and cations of a neutral salt solution. This point is a truer expression of the amphoteric nature of a soil than the cataphoretic isoelectric point (10).

THE MUTUAL "NEUTRALIZATION" OF SOIL MATERIALS

Experimental. The materials used in the main part of our work were taken from a podzol profile, whose A_2 horizon was unusual because of its chalk-white color. The profile was dug near the Häggbygget farm along the road from Rössjöholm to Voxtorp over the Hallandsås ridge in southern Sweden. A brief description follows:

Forest of pine, oak, and birch
Ground vegetation of the vaccinium type
Förna of leaves, pine needles, and twigs
A_0 0–15 cm., consisting of a 4 cm. loose F layer and a 10 cm. compact H layer
A_2 16–27 cm., chalky white
B_1 28–37 cm., crusty irregular layer of very dark brown color of ferric-humate
B_2 38–60 cm., rusty brown
C 61 cm., sand on stony moraine

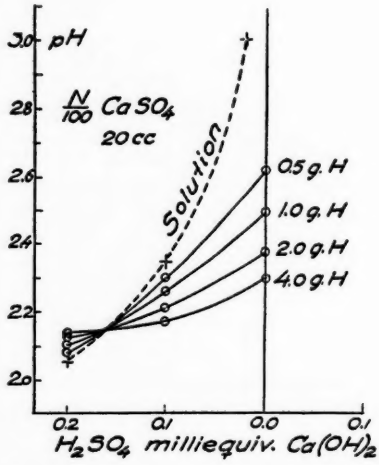


FIG. 49. The equi-ionic point in relation to the ultimate pH at different concentrations of humus (H)

The samples were sifted through a 2 mm. sieve and electrodialyzed. The pH_u in a 0.01 *N* $CaSO_4$ solution was then determined by the quinhydrone electrode. The suspensions were made as concentrated as possible. In this condition, the pH_u will closely approach the equi-ionic point in the same solution. The relationship is brought out in figure 49, which shows the ultimate pH and the equi-ionic point of the humus (H-layer) in the concentrations of 0.5, 1.0, 2.0, and 4.0 gm. in 20 cc. solution. Duplicate determinations gave the following pH_u values:

Humus gm	0.5	1.0	2.0	4.0
pH_u	2.66	2.48	2.37	2.28
	2.60	2.50	2.38	2.21

The pH of the equi-ionic point, that is, the pH where the titration curves of the electrodialyzed humus intersect the solution curve, is, of course, the same for all concentrations of humus and lies in the $CaSO_4$ solution at about pH 2.16.

Although the equi-ionic point is the only true expression of the amphoteric nature of soil colloids, we have, in the following study on the interaction of the materials from the different podzol horizons, confined ourselves to the simple determination of the ultimate pH (6). The dilution effect has been reduced to a minimum by always making the suspensions as concentrated as possible.

The pH_u in 0.01 *N* $CaSO_4$ of the different samples were as follows:

Horizon	F	H	A_2	B_1	B_2	C
pH_u in $\frac{N}{100}$ $CaSO_4$	2.58	2.42	3.27	3.77	4.40	4.52

As shown in a previous work (7) the pH_u increases progressively from the H layer down to the parent material (C). The A horizons represent the zone of eluviation, and the soil complex is here more acidic, i.e., has a lower isoelectric point, than the complex in the B horizons, which together represent the zone of illuviation, i.e., the zone in which the cationic complex, mobilized in A, becomes isoelectric and is precipitated. Material from the A horizons must, therefore, interact with the material from the B horizons when the two are mixed. In the following, we shall call the component which has the lowest pH_u the acidic component, and the other, the basic component. Thus in a mixture of A_2 and B_1 the latter is the basic component, because it will play the part of a base in its interaction with A_2. But in a mixture of B_1 and B_2, B_1 becomes the acidic component, because in its interaction with B_2 it will be its acidic groups which will become engaged.

Figure 50 (*a*), (*b*), and (*c*) shows the relationship between the ultimate pH in a 0.01 *N* $CaSO_4$ solution and the percentage composition of mixtures of $A_2 + B_1$, $A_2 + B_2$ and $A_2 + C$. The curves are all convex to the ordinate axis, which shows that the basic components (B_1, B_2, and C) possess a greater neutralizing power per unit mass than the acidic component. We can also express this by saying that the B and C soils (not necessarily their colloidal fraction) have a lower equivalent weight (as base) than the A_2 soil (as acid). If we calculate the equivalent ratio in each case by dropping a perpendicular from that point on the curve which corresponds to the pH midway between the pH values of the single components, we get the following results:

$$90\ A_2 = 10\ B_1, \qquad 92.5\ A_2 = 7.5\ B_2, \qquad 93.5\ A_2 = 6.5\ C.$$

The power of the basic components to neutralize the acidic component is, therefore,

$$C > B_2 > B_1.$$

The order happens in this particular soil to be the same as that of the ultimate pH, but it must be understood that the two factors are independent of one another. The power of a soil to neutralize acids and bases is strictly a quantitative factor depending on the equivalence of the basic and acidic residues, respectively, whereas the ultimate pH is an intensity factor expressing the relative activity of the acidic and basic groups.

How well the form of the curves agrees with the theory is brought out by

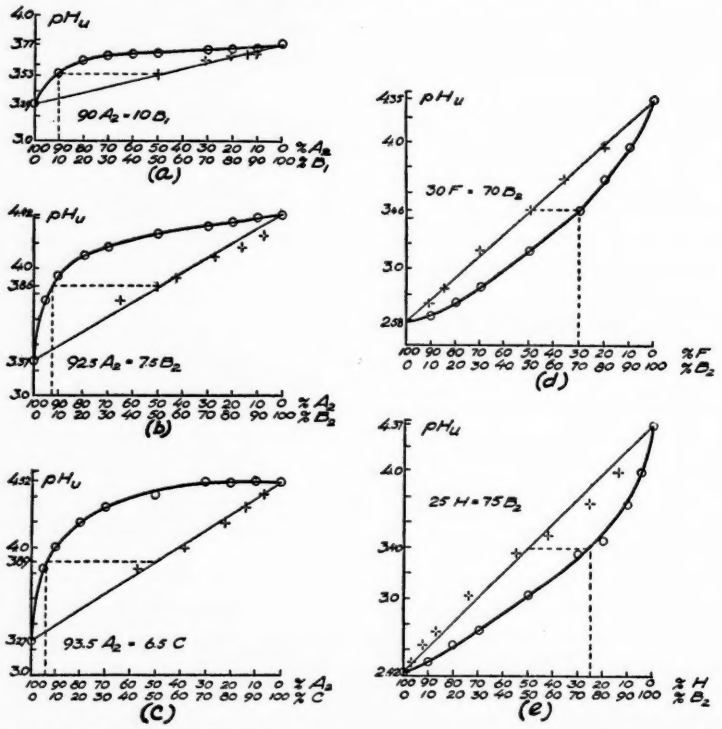


FIG. 50. The ultimate pH of mixtures of various soil components in different proportions. The + points along the straight lines are calculated on the basis of the equivalent proportions.

transforming the weight ratios to equivalence ratios (by dividing the percentages by the corresponding value in the equivalent ratio) and transposing the pH values to the corresponding points. These points should lie on a straight line joining the two ends of the experimental curve, provided that the acid and base neutralization curves of the two soil components have a uniform slope within the range of their mutual interactions, as already explained.

If instead of A_2, as acid component, we use the more acidic humus material

from the F and H layers, we get curves which are concave to the ordinate axis. Figure 50 (*d*) and (*e*) shows the interaction between the H and B_2 and the F and B_2, respectively. The equivalence is 25 H to 75 B_2 and 30 F to 70 B_2.

The results show that the activity (pH_u) as well as the power to neutralize base is greater in H than in F. No exception to this rule has thus far been found by us.

THE TITRATION CURVES OF SOIL MIXTURES

We have seen that different soil materials interact according to the general theory of ampholytes. We shall now study the titration curves of soil mixtures to see to what extent the capacity to bind acid and base is affected by the mixing.

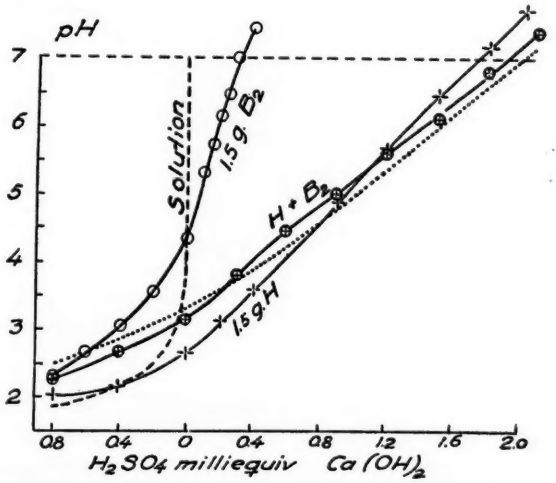


FIG. 51. The titration curves of the podzol B_2 as the basic component, and of H (humus) as the acidic component, when single and when mixed

The titration was carried out in large pyrex test tubes, to which was added 15 cc. 0.04 *N* $CaSO_4$, together with the required amount of H_2SO_4 or $Ca(OH)_2$, and enough water to make a final volume of 60 cc. The soil was then added, and the tubes were stoppered and shaken for 16 hours. The high dilution gave a higher pH_u than in the preceding experiment.

Several combinations have been investigated, but since the results are in general the same in all cases, only two sets of curves will here be shown.

Figures 51 and 52 show the titration curves of H, B_2, and H + B_2, and of B_2, Al-"hydroxide," and B_2 + Al-"hydroxide," respectively. The soil materials H and B_2 were of the electrodialyzed Häggbygget podzol, and the Al-"hydroxide" was an untreated commercial product. The proportions were

as noted in the figures. The dotted curves represent the theoretical, net amount of base and of acid in combination in the mixture, and are plotted from the $\Sigma x - y$ (Σbase $-$ acid) of the single components as in the theoretical curves in figure 48.

If the amphoteric soil colloids obeyed the laws of ideal ampholytes, then the experimental and theoretical curves of the mixtures should coincide, and the basic component should neutralize the acidic component according to its capacity to neutralize acid at the particular pH, and should, therefore, not bind any of the acidic component above its isoelectric point. The same applies to the acidic component, which should not bind any of the basic component below its isoelectric point.

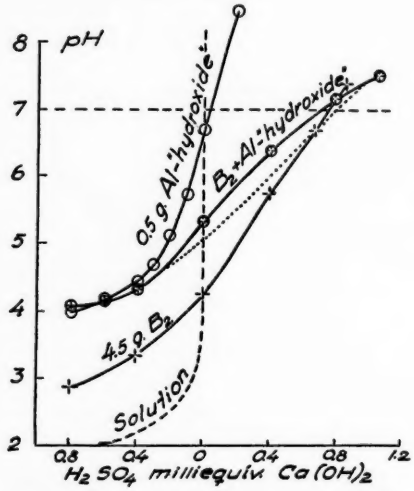


FIG. 52. The same as fig. 51, but with A1 "hydroxide" as the basic component, and the B_2 as the acidic component

But colloids which form slightly dissociated salts continue to bind anions above, and cations below, their isoelectric point. Soil colloids adsorb more SO_4 than Cl ions at the equi-ionic pH. For the same cation, this pH lies, therefore, higher in sulfate than in chloride solutions. The PO_4 ion, and the colloidal anions of the soil, form still less dissociated compounds, and unite, therefore, with the basic residue of the soil complex up to very high pH. The less dissociated the compound (the salt), the stronger the acidic or basic residue appears to be, or, mathematically stated, the greater is the apparent acid or base dissociation constant. For this reason there can be no fixed equi-ionic point in colloids. This point must vary with the ionic environment.

The general tendency is, therefore, for the experimental curve to lie above

the theoretical curve on the alkaline side, and below it on the acid side. This means that the capacity of the mixtures to bind base and acid has been reduced more than the "theoretical" amount, which again means that the mutual neutralization of the acidic and the basic components has gone further than it would in the case of soluble ampholytes. This is exactly what one might have expected because of the slight dissociation of the products (alumino and ferric-silicates, humates, etc.) formed. The compounds formed are however, subject to a hydrolytic decomposition at sufficiently high and low pH values. The two curves appear in general to join each other between a pH of 7 and 8. The ease with which the complex undergoes a hydrolytic cleavage will depend upon the conditions. Drying and aging will doubtless lead to a more stable compound.

It is more difficult to explain why the intersection of the experimental and theoretical curves does not in every case occur at the theoretical zero position. This happened only twice in the seven combinations investigated. In three cases the intersection occurred on the alkaline side, as in figure 51, and in two cases it occurred on the acid side, as in figure 52. It appears as if the acidic and basic components did not neutralize each other to an equivalent extent. We shall not attempt to give a definite explanation for this anomaly, if it really exists, but merely point out that the observed phenomena would result, if one of the components combined with the less active groups of the other component, instead of with the most active groups, as would be the case between soluble ampholytes. If the dissociation of the compound is low enough, the basic component might engage the weakest acidic groups and leave the stronger ones free, or vice versa. The complexity of the materials opens the way to many anomalies.

THE CA EQUIVALENT

The capacity of the basic component to neutralize the acidic component can be expressed in terms of its Ca equivalent. This can be read off directly from the curves in figures 51 and 52 for the particular proportions here used. It is obvious that the Ca equivalent per unit weight of the basic component of a mixture is far greater in smaller than in larger increments.

PRACTICAL APPLICATION

One of the most obvious practical applications of the mutual interaction of soil materials is in connection with the cultivation of podzolized soils. If, by deep digging or plowing, material of the B horizons is incorporated with the material of the very acid, eluviated upper horizons, it will result in a soil which (*a*) has a higher isoelectric point and is less acidic, (*b*) requires less lime, (*c*) contains more mineral colloids, (*d*) contains more PO_4 and other nutrients, (*e*) stimulates the microbial activity and brings about a more rapid mineralization of the raw humus, thus also indirectly elevating the pH.

The last mentioned factor is now being investigated.

EXCHANGE ACIDITY, EXCHANGE ALKALINITY, AND THE POINT OF EXCHANGE NEUTRALITY

It is well known that the addition of a neutral salt to a soil suspension generally causes a lowering of the pH. The cations of the salt displace the H ions of the complex, resulting in the so-called exchange acidity, and the greater the amount of the salt added the greater is the lowering of the pH. But this exchange acidity results only when the pH of the suspension is above the point of exchange neutrality of the soil. If the pH lies below this point, then the displacement of the OH ions of the complex by the anions of the salt predominates, resulting in an elevation of the pH, i.e., an exchange alkalinity, which is greater the higher the concentration of the salt.

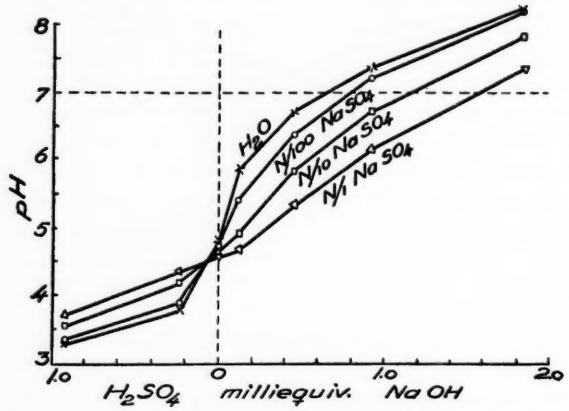


FIG. 53. Titration curves of an electrodialyzed soil (from a podzol profile, B_2 horizon) in water and in salt solutions. 10 gm. soil in 20 cc. solution. The curves intersect at the equi-ionic point

If, therefore, we titrate a soil in the absence of a salt, on the one hand, and in the presence of a high concentration of the salt, on the other, we get two titration curves, which intersect each other at a point where the effect produced by the increase in the anion concentration is balanced by the effect produced by the increase in the cation concentration, that is, at the point where the salt, as a whole, produces no apparent effect. This point is the point of exchange neutrality.

Figure 53 shows the curves obtained by the electrometric titration of a 10 gm. electrodialyzed B_2 sample of the Häggbygget podzol by NaOH and H_2SO_4, in water and in the presence of 0.01 *N*, 0.1 *N*, and 1.0 *N* Na_2SO_4 (10).

In the case of soluble ampholytes, which form completely dissociated salts, the capacity to bind acid and base would be the same for all acids and bases, and the addition of a neutral salt solution would produce no special effect beyond the activity effect. But the ampholytoids form slightly dissociated

salts. They are, therefore, not only *weak acids and bases;* they are also "weak salts." When an acid of this type combines with a base few anions are formed to suppress the dissociation of the acid. For this reason, the acid acts as if it were a stronger acid than it really is, that is, *the apparent dissociation constant of the acid is greater than the true constant.* The effect is greater the lower the dissociation of the salt. Thus it is greater in the Ca complex than in the K complex, and greater in the latter than in the Na complex, because the divalent Ca ion is less dissociated than the monovalent ions, and among the latter the least hydrated K ion is also the least dissociated. The effect is still greater in the presence of neutral salts, for then the dissociation of the colloidal salt is greatly suppressed, whereas the dissociation of the colloidal acid suffers a correspondingly smaller suppression. This will explain why a soil, as acid and as base, has different apparent dissociation constants and a different equi-ionic point[2] in different solutions.

TABLE 147

Theoretical capacity to neutralize base (x) *and acid* (y) *when*: (A) $k_a = 1 \times 10^{-5}$; $k_b = 1 \times 10^{-11}$

$\frac{[H^+]N}{[OH^-]N}$	$\frac{10^{-0}}{10^{-14}}$	$\frac{10^{-1}}{10^{-13}}$	$\frac{10^{-2}}{10^{-12}}$	$\frac{10^{-3}}{10^{-11}}$	$\frac{10^{-4}}{10^{-10}}$	$\frac{10^{-5}}{10^{-9}}$	$\frac{10^{-6}}{10^{-8}}$	$\frac{10^{-7}}{10^{-7}}$	$\frac{10^{-8}}{10^{-6}}$
x				0.01	0.09	0.50	0.91	0.99	1.00
y	1.00	0.99	0.91	0.50	0.09	0.01			
$x - y$	−1.00	−0.99	−0.91	−0.49	0.00	0.49	0.91	0.99	1.00

(B) $k_a' = 1 \times 10^{-4}$; $k_b' = 1 \times 10^{-10}$

x'			0.01	0.09	0.50	0.91	0.99	1.00	1.00
y'	1.00	1.00	0.99	0.91	0.50	0.09	0.01		
$x' - y'$	−1.00	−1.00	−0.98	−0.82	0.00	0.82	0.98	1.00	1.00

The neutral salt effect is, therefore, no mysterious form of adsorption, but is simply an expression of the principle mathematically expressed in equation (B) and graphically illustrated in figure 41. This is made quite evident by the following theoretical reconstruction of the experimental curves.

Let us assume that the soil complex has the apparent acid dissociation constant $k_a = 10^{-5}$ and the base constant $k_b = 10^{-11}$ when combining with a certain strong base and acid, respectively. The capacity to bind base (x) and acid (y) is shown in table 147 (A). At pH 4.0 ($[H^+] = 10^{-4}$) $x - y = 0$. This we define as the equi-ionic point.[3] Let us now assume that the apparent constants of the colloid are $k_a' = 10^{-4}$ and $k_b' = 10^{-10}$ when combining

[2] The pH at which the soil binds equal quantities of acid and base.

[3] It would be the isoelectric point only in the case of true ampholytes which form completely dissociated salts, and in the case of colloids if the degree of anionic and cationic dissociation happens to be the same.

with the same acid and base, but in the presence of a certain concentration of the neutral salt. We get then the capacities x' and y' shown in table 147 (B). The equi-ionic point would, in this case, still be at pH 4.0, but the capacity to bind acid and base at this point has increased from 9 to 50 per cent of the total capacities.

If we plot the individual values of x and y of the two ampholytes against the pH, we get the dotted curves shown in figure 54. These curves express the *absolute* capacity of the basic group to bind acid (y) and of the acidic group to bind base (x). By plotting the $x - y$ values we get the full drawn curves in the figure. These curves express the *net* capacity to bind acid and

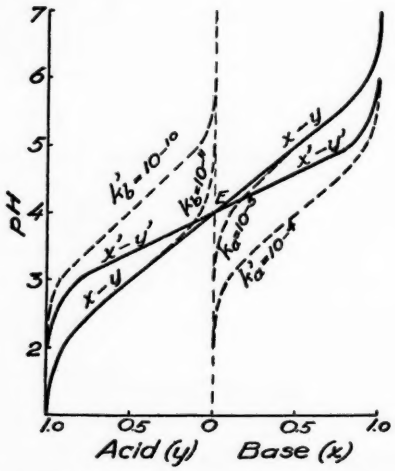


FIG. 54. Theoretical capacities of the basic and acidic groups of the soil complex to bind acid (y) and base (x) when the apparent dissociation constants are assumed to be k_b and k_a in water, and k_b' and k_a' in a salt solution (broken lines); and the corresponding net capacities, $x - y$ and $x' - y'$, of the soil to bind acid (negative values) and base (positive values). E = Equi-ionic point (cf. table 147)

base. We note that the latter curves intersect each other (at E or at pH 4.0) just as the water curve and salt solution curves of the soil in figure 53 intersect.

The phenomenon of exchange acidity, exchange alkalinity, and of the point of exchange neutrality is thus placed in a new light, in which the chemistry of the reaction becomes comprehensible and clear.

In the experimental curves the individual values of x and y, that is, the *absolute* capacities of the acidic group to bind base, and of the basic group to bind acid, are not shown. The experimental curves represent the $x - y$ values and show only the *net* capacity to bind acid and base. The values obtained by titrating the electrodialyzed soil in water may be put equal to the absolute capacities if we ignore the mutual interaction of the acidic and basic

groups of the complex, i.e., the formation of an inner salt. In the presence of a salt, the saturation of the soil with anions and cations may be considerable at the equi-ionic point, where the net saturation is zero, but the experimental curves give no information as to the magnitude of this saturation.

The double adsorption of the anions and the cations of the salt at, and near, the equi-ionic point expresses itself in a flattening of the curve near this point or, which is the same thing, in a greater buffer effect. The reason for this increase in the buffer effect in the presence of salt is best seen in figure 54. Thus if a soil, already highly saturated with anions and cations at the equi-ionic point through the influence of a high salt concentration, be titrated with a base, then the latter will be consumed, partly in desaturating the soil of its anions and partly by the direct neutralization, as illustrated by the following equation, in which A·B represent the colloidal complex:

$$\begin{matrix} Na \cdot \\ H \cdot \end{matrix} A \cdot B \begin{matrix} \cdot OH \\ \cdot Cl \end{matrix} + 2\ NaOH \rightarrow \begin{matrix} Na \cdot \\ Na \cdot \end{matrix} A \cdot B \begin{matrix} \cdot OH \\ \cdot OH \end{matrix} + NaCl + H_2O.$$

In the absence of salt, the neutralization of the completely unsaturated soil would take place as follows:

$$\begin{matrix} H \cdot \\ H \cdot \end{matrix} A \cdot B \begin{matrix} \cdot OH \\ \cdot OH \end{matrix} + 2\ NaOH \rightarrow \begin{matrix} Na \cdot \\ Na \cdot \end{matrix} A \cdot B \begin{matrix} \cdot OH \\ \cdot OH \end{matrix} + 2\ H_2O.$$

It is thus seen that the total capacity to bind base (or acid) is the same no matter what the degree of saturation might be at the equi-ionic point. It also follows, from an inspection of figure 54, that the net capacity to bind cations becomes equal to the absolute capacity at a point where the soil no longer binds *anions*, or vice versa. This is in agreement with the results obtained by titrating the soil in Na_2SO_4 and NaCl solutions. The capacity to bind base at pH 7.0 was practically the same although the point of exchange neutrality was 0.52 pH higher in the sulfate solution.

For a detailed discussion the reader is referred to the original paper (9) and to a forthcoming paper (XX) in this series, in which the relationship between the point of exchange neutrality and the equi-ionic point, under different conditions, is brought out.

SUMMARY

The theory of the interaction of colloidal hydroxides with colloidal and soluble acids has been discussed, and two forms of isoelectric precipitates have been accounted for.

By determining the ultimate pH and the titration curves of electrodialyzed samples, when single and when mixed, it has been shown that soils having different isoelectric points (or pH of exchange neutrality) interact in a general way according to the theory of ampholytes. In the case of amphoteric colloids the mutual neutralization proceeds, however, further, because of the limited dissociation of their salts.

The chemistry of exchange acidity, exchange alkalinity, and of the point of exchange neutrality has been expounded.

The reactions of the soil colloidal complex are fundamentally the same as the reactions of ordinary weak electrolytes, and can be accounted for by a special application of the known laws of ordinary weak acids and bases, and of ampholytes.

REFERENCES

(1) FREUNDLICH, H. 1922 Kapillarchemie, ed. 2. Leipzig.

(2) GRAHAM, TH. 1865 Über die Eigenschaften der Kieselsäure und andere analogen Colloïdsubstanzen. *Liebigs Ann. Chem.* 135: 67.

(3) MATTSON, SANTE 1930 The laws of soil colloidal behavior: III. Isoelectric precipitates. *Soil Sci.* 30: 459–495.

(4) MATTSON, SANTE 1931 The laws of soil colloidal behavior: IV. Isoelectric precipitates. *Soil Sci.* 31: 57–77.

(5) MATTSON, SANTE 1931 The laws of soil colloidal behavior: V. Ion adsorption and exchange. *Soil Sci.* 31: 311–331.

(6) MATTSON, SANTE 1931 The laws of soil colloidal behavior: VI. Amphoteric behavior. *Soil Sci.* 32: 343–365.

(7) MATTSON, SANTE, AND GUSTAFSSON, Y. 1934 The chemical characteristics of soil profiles: I. The podzol. *Ann. Agr. Col. Sweden.* 1: 33–68.

(8) MATTSON, SANTE, AND GUSTAFSSON, Y. 1935 The chemical characteristics of soil profiles: II. The mutual interactions of podzolic material. Ann. Agr. Col. Sweden. 2: 1–30.

(9) MATTSON, SANTE, AND GUSTAFSSON, Y. 1935 The neutral salt reaction in relation to the point of exchange neutrality, the saturation and combining capacity of a soil. Ann. Agr. Col. Sweden. 2: 136–157.

(10) MATTSON, SANTE, AND HESTER, J. B. 1932 The laws of soil colloidal behavior: X. Exchange neutrality and combining capacity. *Soil Sci.* 34: 459–482.

(11) MICHAELIS, L. 1926 Hydrogen Ion Concentration. Baltimore.

THE LAWS OF SOIL COLLOIDAL BEHAVIOR: XIX. THE GEL AND THE SOL COMPLEX IN SOIL FORMATION

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In the preceding article of this series (10), a distinction was made between the anionic and cationic *sol* complexes which arise on the alkaline and acid side of the isoelectric point of the *gel* complex. We shall now present the results of experiments, carried out in an effort to establish the laws of the formation, composition, and behavior of the anionic and cationic sol complexes.

EXPERIMENTAL: THE GEL AND THE SOL COMPLEX

In a previous work, published elsewhere (11), we offered an explanation of the dispersion and precipitation within the podzol profile. The facts established were in complete accordance with the laws of isoelectric precipitation and with the theory of isoelectric weathering. But the limited conditions of our former experiments were such that we could only predict, but not show, the important fact that, even in the case of the natural soil material, there must be a minimum in dispersibility at a pH which corresponds to the isoelectric point.

In the work referred to, we studied the composition and amphoteric behavior of the sol complex obtained in the extracts (pH 3.2 to 3.7) from a series of mixtures of a mineral soil with various proportions of humus. Since only one extract was prepared from each mixture, we decided to continue the work by studying each mixture in series of varying pH. We are here presenting the result of this work. The materials used and the method employed follow.

Samples of 200 gm. of the B_2 horizon of the previously described Häggbygget podzol (10) were shaken for 15 hours, in a total volume of 2 l., in 20 × 30 cm. hot water bags together with the following quantities of humus from the H-layer of the same profile:

Series I	None
II	12.5 gm.
III	25.0 gm.
IV	50.0 gm.
V	100.0 gm.

Each series consisted of eight extractions which differed from one another in the amount of NaOH or HCl added to cover a range of pH from about 3 to 7. In order to have a fairly uniform concentration of electrolyte in each mixture,

NaCl was added in such an amount that the sum NaCl + NaOH or NaCl + HCl was never less than 20 m.e. in 2 l. The shaking was done for 7 hours the first day, 7 hours the second day, and 1 hour the third day. The rubber bags proved excellent for this work.

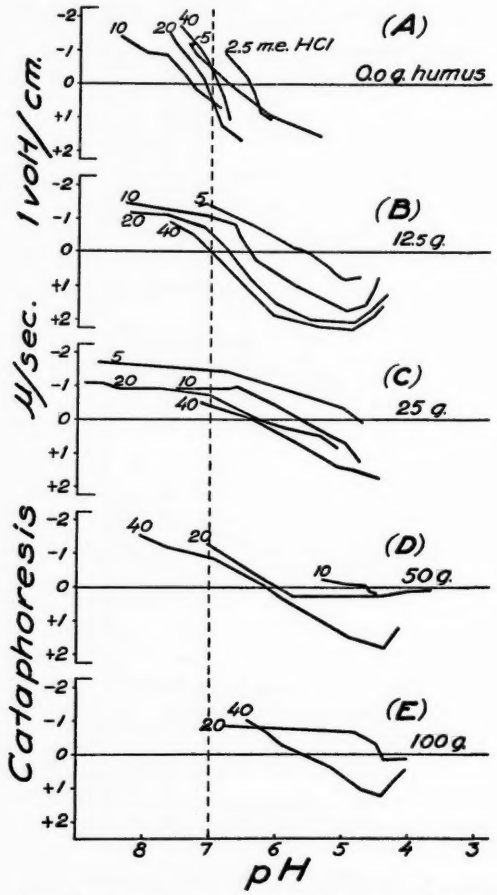


FIG. 55. The electrophoresis and isoelectric point of the extracted complex in relation to the acidity (m.e. HCl) and amount of humus added to 200 gm. of soil.

In addition to the soil + humus series, a series containing 25 gm. humus alone was used.

The extracts were filtered through a triple layer of 11 cm. no. 00 Berzelius filters in Büchner funnels. The edges of the wet papers were sealed to the porcelain by adding some melted paraffin and rotating the inclined funnel until

the paraffin lost its fluidity. The funnel was then placed in the suction flask, and the filter was sucked tight to the bottom until the paraffin was quite hard. After pouring back the first portion of the filtrate, which sometimes was slightly turbid, we were able to obtain clear extracts.

The extracts were examined as follows:

(*A*) *The color.* The extracts were nearly colorless in the neighborhood of the isoelectric point of the mixture. At higher and lower pH the color became yellow and then brown.

(*B*) *The pH.* This was determined by the quinhydrone method.

(*C*) *Flocculation and electrophoresis.* 50 cc. portions of an extract are placed in a series of large test tubes, usually about 10 to 12 tubes. In a preliminary test, the quantity of NaOH or HCl required to produce the most rapid flocculation, if any, is determined. This quantity is then added to one of the tubes in the middle of the series. In one direction, this quantity is progressively decreased until no flocculation is observed, and in the other direction, it is increased until the sol again fails to flocculate, or until a certain amount has been added. The following day 20 cc. of the liquid in each tube

TABLE 148

Flocculation, pH, and cataphoresis of extracts

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10
Flocculation.....	0	X	XX	XXX	XXXX	XXXX	XXXX	XX	X	0
pH.....	3.03	3.90	4.64	4.85	5.20	5.59	6.12	6.60	7.10	8.04
μ/sec. 1 volt/ cm.....	—	+1.96	+1.33	+0.86	+0.24	±0.0	−0.26	−1.03	−2.12	—

is withdrawn for pH determination. The precipitate is then suspended in the remaining liquid by inverting the tubes, and the electrophoresis is determined by the ultramicroscopic method as previously described (5). The isoelectric point is found by interpolation, when not directly observed (cf. fig. 55).

One such series, consisting of 10 tubes, is shown in plate 3. The data obtained for this series are given in table 148.

The flocculation is designated by X's, one X signifying slight, and four X's complete, flocculation. The electrical migration of the particles has been reduced to μ per second, in a potential gradient of 1 volt per centimeter. It will be noted that the sol flocculated completely in only three of the tubes: at pH 5.20, 5.59, and 6.12, and that the floc was isoelectric at pH 5.59, i.e., in the sixth tube from the left.

(*D*) *Organic matter.* This is put equal to the loss on ignition after 16 per cent of the weight of silica and sesquioxides, assumed as water lost by the inorganic gels, is subtracted. It was determined by evaporating 500 cc. of the extract, drying at 105°C., and igniting at dull redness in the electric furnace.

(*E*) *Silica and sesquioxides.* These were determined in the ignited ash in

TABLE 149

The composition and isoelectric point of the sol complex, extracted at different pH from different mixtures of soil and humus

200 gm. soil in 2 l.

Series I. No humus

M. E. ADDED	NaOH			HCl				
	10	4	0.0	2.5	5	10	20	40
pH of extract	6.39	5.29	4.72	4.40	4.04	3.84	3.41	3.13
Isoelectric pH	no floc.	no floc.	no floc.	6.42	6.75	7.30	7.10	6.94
m.e. NaOH required*	.....	.....	.....	2.0	4.5	9.4	19.2	38.6
Organic matter (gm.)	0.526	0.153	0.073	0.124	0.152	0.221	0.364	0.888
SiO_2 (gm.)	0.0088	0.0080	0.0032	0.0048	0.0067	0.0134	0.0244	0.0496
Al_2O_3 (gm.)	0.0456	0.0251	0.0224	0.0594	0.1088	0.1800	0.3527	0.6668
Fe_2O_3 (gm.)	0.0208	0.0062	0.0016	0.0008	0.0028	0.0040	0.0045	0.0172
Org. mat. (gm.) ÷ M_2O_3 (millimols)	0.92	0.54	0.32	0.21	0.14	0.12	0.11	0.13
SiO_2/M_2O_3	0.25	0.47	0.23	0.14	0.10	0.12	0.11	0.12

Series II. 12.5 gm. humus

M. E. ADDED	NaOH			HCl				
	15	6	0.0	2.5	5	10	20	40
pH of extract	6.97	5.65	4.75	4.31	3.99	3.62	3.33	2.95
Isoelectric pH	no floc.	no floc.	no floc.	no floc.	5.55	6.40	6.70	7.00
m.e. NaOH required*	.....	.....	.....	.....	2.6	7.3	17.2	36.0
Organic matter (gm.)	0.686	0.287	0.152	0.205	0.195	0.280	0.514	0.852
SiO_2 (gm.)	0.0084	0.0116	0.0048	0.0076	0.0108	0.0176	0.0272	0.0708
Al_2O_3 (gm.)	0.0348	0.0192	0.196	0.0452	0.1038	0.1604	0.3111	0.6532
Fe_2O_3 (gm.)	0.0136	0.0048	0.0000	0.0008	0.0030	0.0032	0.0037	0.0168
Org. mat. (gm.) ÷ M_2O_3 (millimols)	1.61	1.32	0.80	0.46	0.19	0.18	0.17	0.13
SiO_2/M_2O_3	0.33	0.88	0.41	0.28	0.17	0.18	0.15	0.18

Series III. 25 gm. humus

M. E. ADDED	NaOH			HCl				
	20	8	0.0	2.5	5	10	20	40
pH of extract	6.89	5.51	4.60	4.31	3.98	3.70	3.35	2.98
Isoelectric pH	anionic	no floc.	no floc.	no floc.	4.75	5.61	6.30	6.32
m.e. NaOH required*	.....	.....	.....	.....	2.0	4.3	14.0	33.3
Organic matter (gm.)	0.972	0.448	0.226	0.233	0.308	0.311	0.526	1.186
SiO_2 (gm.)	0.0168	0.0196	0.0100	0.0104	0.0236	0.0328	0.0328	0.0624
Al_2O_3 (gm.)	0.0509	0.0268	0.0191	0.0232	0.0369	0.1080	0.2788	0.6267
Fe_2O_3 (gm.)	0.0179	0.0064	0.0009	0.0009	0.0031	0.0036	0.0036	0.0173
Org. mat. (gm.) ÷ M_2O_3 (millimols)	1.60	1.48	1.17	1.00	0.81	0.29	0.19	0.19
SiO_2/M_2O_3	0.46	1.07	0.86	0.74	0.63	0.50	0.20	0.17

TABLE 149—*Concluded*

Series IV. 50 gm. humus

M. E. ADDED	NaOH			HCl				
	30	12	0.0	2.5	5	10	20	40
pH of extract.....	6.87	5.38	4.29	4.31	3.99	3.69	3.31	2.92
Isoelectric pH.....	anionic	no floc.	no floc.	no floc.	no floc.	4.63	5.98	6.06
m.e. NaOH required*.	.....	.....	.....	.....	.....	1.8	10.7	29.8
Organic matter (gm.)	1.464	0.688	0.382	0.380	0.380	0.443	0.676	1.145
SiO_2 (gm.).....	0.0240	0.0232	0.0148	0.0176	0.0240	0.0332	0.0376	0.0664
Al_2O_3 (gm.).....	0.0594	0.0348	0.0231	0.0232	0.0288	0.0841	0.2052	0.5512
Fe_2O_3 (gm.).....	0.0198	0.0080	0.0009	0.0012	0.0032	0.0031	0.0032	0.0160
Org. mat. (gm.) ÷ M_2O_3 (millimols)...	2.08	1.77	1.65	1.62	1.26	0.53	0.33	0.21
SiO_2/M_2O_3.....	0.56	0.99	1.06	1.24	1.32	0.65	0.31	0.20

Series V. 100 gm. humus

M. E. ADDED	NaOH			HCl				
	40	20	0.0	2.5	5	10	20	40
pH of extract.....	6.80	5.28	4.08	3.90	3.75	3.53	3.31	2.93
Isoelectric pH.....	anionic	anionic	no floc.	no floc.	no floc.	no floc.	4.37	5.60
m.e. NaOH required*.....	.....	.....	.....	.....	.....	.....	4.0	22.4
Organic matter (gm.).....	2.105	1.289	0.777	0.672	0.698	0.704	0.881	1.364
SiO_2 (gm.).....	0.0390	0.0372	0.0220	0.0312	0.0304	0.0372	0.0456	0.0692
Al_2O_3 (gm.).....	0.0890	0.0624	0.0248	0.0290	0.0410	0.0539	0.1241	0.4117
Fe_2O_3 (gm.).....	0.0240	0.0124	0.0012	0.0010	0.0026	0.0017	0.0019	0.0115
Org. mat. (gm.) ÷ M_2O_3 (millimols).	2.06	1.87	2.10	2.32	1.67	1.31	0.72	0.33
SiO_2/M_2O_3.....	0.63	0.89	1.45	1.79	1.21	1.14	0.62	0.28

* To render the complex isoelectric.

the usual manner. The results are shown in table 149 and in figures 55 to 61.

The results of the experiment, which agree in general with the theory outlined, are as follows:

(*a*) There is a minimum in the amount of material dispersed at a pH which corresponds to the isoelectric point of the gel complex formed in the mixture. The B_2 soil material is rich in sesquioxides and has, therefore, a relatively high isoelectric point. The addition of humus suppresses the cationic ionization of the complex, thereby lowering the isoelectric point, together with the point of maximum stability. This is clearly illustrated in figures 56, 57, and 58.[1]

(*b*) On the acid side of the points of minima, the sol complex is cationic, being isoelectrically precipitated by the addition of alkali (cf. fig. 55). The

[1] For the sake of clearness, only four of the series are included in the figures.

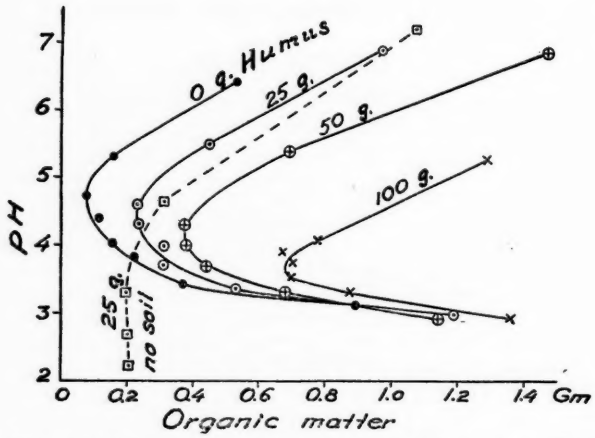


FIG. 56. The relation between the pH and organic matter in the extracts. The figures on the curves give the amount of humus added to 200 gm. of soil.

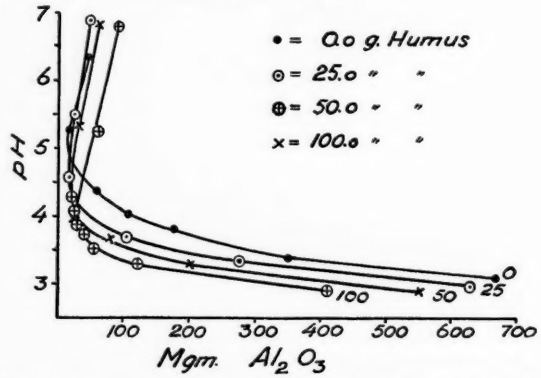


FIG. 57. The relation between the pH and Al_2O_3 in the extracts of the different series.

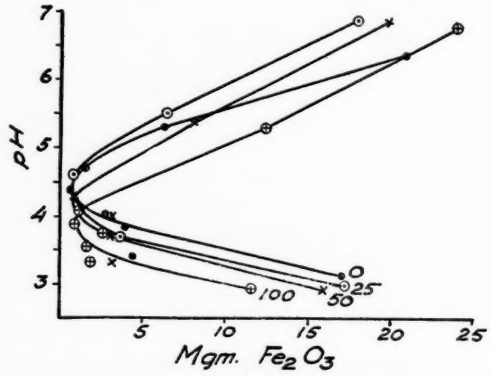


FIG. 58. The relation between the pH and Fe_2O_3 in the extracts of the different series.

absolute amount of acidic, as well as basic, material dispersed, increases progressively as the pH is lowered, but the proportion of basic material becomes greater, and the isoelectric point of the sol complex becomes higher, the lower the pH of the extract. This is because the hydrolysis is more complete the lower the pH, resulting in a cationic sol complex, in which relatively little humic and silicic acid remain associated. This is shown in the table by the ratios of organic matter and of silica to sesquioxides.

(*c*) At pH above the points of minima, the sol complex is anionic, but is incompletely precipitated by HCl, and only in the more concentrated, dark colored extracts obtained at high pH. The precipitation was more complete in the presence of Ca, but the complex remained electronegative throughout the usual range of isoelectric precipitation; there was no isoelectric point, the proportion of humus being too high.

Although the absolute quantities of dispersed Al and Fe increase again at higher pH, because of their association with humic acid, the anionic sol complex becomes richer in acidic material with an increase in the pH of the extract, as a result of a progressive hydrolysis.

To sum up points (a), (b), and (c), we find that the soil complex is most stable at its isoelectric point; that there is an absolute increase in the acidic and basic material dispersed on either side of this point, but that on the acid side the sol complex, which is cationic, becomes progressively richer in basic material, whereas on the alkaline side the sol complex, which is anionic, becomes progressively richer in acidic material. This is all in complete agreement with the theory of isoelectric weathering.

The nearer the isoelectric pH of the cationic sol complex approaches the pH of the extract, the smaller is the amount of alkali required to render the complex isoelectric (cf. fig. 59), and the smaller also is the amount of material dispersed, whereas the acidoid /basoid ratio grows larger. At the point where the two pH values coincide, there is no alkali required, and there can, of course, be no isoelectrically precipitable quantities of the amphoteric complex in the extract because, being isoelectric in the mixture, it was never dispersed beyond a certain amount representing, perhaps, the "solubility product" of the complex. As to the acidoid/basoid ratio in the extract at this point, it might be assumed that this represents the composition of the gel complex in the mixture. For if a complex with a lower ratio is cationic, and a complex with a higher ratio is anionic, at this pH, then the gel complex must here, where it is neither anionic nor cationic, not only be isoelectric but must also have a composition which corresponds to that of the extract at this point. It will be noted that the ratios of organic matter and of silica to sesquioxides at the points of minima increase progressively from systems in series I to V.

Since the extracts obtained at, and in the neighborhood of, the minima yield no precipitate, and since the minima are rather diffuse, the isoelectric point of the gel complex is not sharply defined. But apart from the position of the

minima, we get another index in regard to the position of these points by extrapolating the curves in figure 59, representing the amount of alkali required to render the cationic sol complex isoelectric. This amount equals zero at the point where the pH of the extract coincides with the isoelectric pH of the complex. These curves point, therefore, like fingers, to the isoelectric pH of the respective systems. The isoelectric point of the gel complex in the different systems may thus be estimated to lie between, let us say, pH 3.5 and 4.8. This agrees well with the amphoteric behavior of the two components as previously reported (9, 10).

The fact that the minima for the different constituents, humus, Al_2O_3, and Fe_2O_3, do not agree so well need not surprise us. The amphoteric complex can, as a unit aggregate, have only one isoelectric point, but it must be remembered

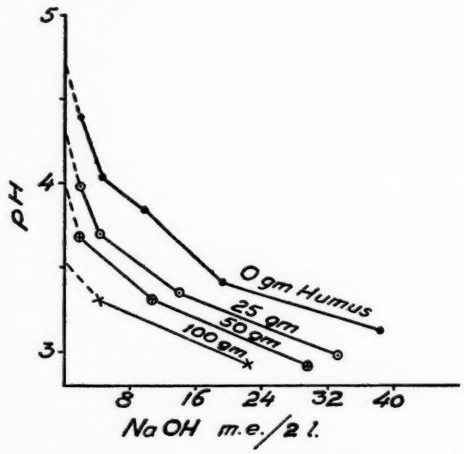


FIG. 59. The relation between the pH of the extracts and the amount of NaOH required for the isoelectric precipitation.

that it has a composite make-up, possessing a mosaic of acidic and basic groups, each ionizing according to its own activity, without regard to the isoelectric point of the aggregate, and only collectively determining the position of this point.

Organic matter. The functions of the humus are as follows:

It lowers the isoelectric point of the complex (cf. the position of the curves in fig. 55, and the minima in fig. 56).

It suppresses the solubility of Al and Fe to a lower pH (cf. lower sections of curves in figs. 57 and 58).

It carries Al and Fe in dispersion, in the form of an anionic complex, at higher pH (cf. upper sections of curves in figs. 57 and 58).

Its nature and its degree of humification affect the above functions. Thus the finely divided organic matter (F_o) of the ground vegetation from the same

podzol profile (Vaccinium type) caused a greater solution of Al and Fe at low pH than the humus (H). Electrodialysis of the F_o material yielded 30.8 m.e. bases and 17.9 m.e. dialyzeable acids per 100 gm., whereas the H material yielded only 8.4 and 1.86 m.e., respectively. We must conclude that it is the colloidal humic acids which fix Al and Fe and protect them from solution at low pH, whereas it is the diffusible acids which are responsible for the ionization and dispersion of these bases. The interaction of the various forms of organic matter with the mineral complex is an important problem which deserves a thorough investigation.

It will be noted that the lower sections of the curves in figure 56 are close together. The system to which no humus was added yields about as much cationically dispersed humus as the other systems. An investigation, recently carried out by Dr. Boratynski in our laboratory, has shown that practically all the cationically dispersed humus comes from the B_2 complex, and not from the added humus. This points to a fundamental difference between soil humus and peat humus. The compound formed during the shaking between the soil complex and the added humus is easily hydrolyzed, so that very little of this humus is carried in dispersion by Al and Fe, whereas the soil humus, precipitated in nature, is firmly bound in the B_2 horizon. This is again reflected by the upper section of the O-curves in figures 57 and 58, which tends to intersect the other curves. This means that the Al and, especially, the Fe are more firmly bound to the soil humus than to the added humus. The former carries relatively more Fe and Al in dispersion than the latter. The difference between the two combinations seems to be the same as the difference between the synthetic and natural alumino-silicates. The question will be discussed in a forthcoming publication.

Aluminum and iron. The functions of Al and Fe may be summarized as follows:

They elevate the isoelectric point of the complex.

They carry humus and silica in dispersion, in the form of a cationic complex. This is strikingly shown in figure 56. The broken curve represents a system containing 25 gm. humus but no soil. We note that there is here no appreciable increase in the dispersion of humus at low pH. The slight increase might be due to the effect of the small amounts of sesquioxides present, or it might be due to the amphoteric nature of the humus itself.

The difference in behavior between Al and Fe is of fundamental importance. We know from previous work (6) that the ferric compounds have a lower isoelectric point than the aluminum compounds of corresponding composition. Iron requires, accordingly, a lower pH for its cationic dispersion, and appeared in appreciable amounts only in the most acidic extracts, round a pH of 3, whereas Al began to increase at from one half to one pH unit higher. At the minima, there are mere traces of iron present, the quantities being about 20 times smaller than those of aluminum. (Note the difference in scale in figs. 57 and 58.) This all points to a greater stability of the ferric humates. This

conclusion is supported by the reversed order of dispersibility in the anionic complex, in which the iron shows a relatively greater increase than aluminum. (Cf. the upper sections of the curves in figs. 57 and 58.) It should be mentioned that ferrous humates have higher isoelectric points than even aluminum has. Ferrous iron is, therefore, cationically dispersed at still higher pH, but this question will be discussed in connection with the aforementioned work of Boratynski.

Silicic acid. The functions of silicic acid are obscured by those of humus, which is present in far greater amounts. It can, however, be said that, like humus, it lowers the isoelectric point of the complex and suppresses the solubility of Al and Fe to a lower pH.

On the basis of other experiments it does not seem to carry Al and Fe in dispersion at pH above the isoelectric point of the gel complex, at least not to any appreciable extent.

TABLE 150

Silica and sesquioxides dissolved at various pH from 20 gm. electrodialyzed Ancylus clay

	M. E. ADDED	pH	SiO_2	Al_2O_3	Fe_2O_3	$\frac{SiO_2}{M_2O_3}$	$\frac{Al_2O_3}{Fe_2O_3}$
			gm.	*gm.*	*gm.*		
HCl.....	4.0	3.4	0.0372	0.0365	0.0041	1.61	14.0
HCl.....	2.0	3.85	0.0281	0.0141	0.0022	3.06	10.1
HCl.....	1.0	4.58	0.0246	0.0032	0.0014	10.20	3.4
HCl.....	0.0	7.3	0.0224	none	none		
NaOH.....	2.0	7.7	0.0165	none	none		
NaOH.....	4.0	7.8	0.0134	none	none		
NaOH.....	8.0	>9.6	0.0197	trace			
$Ca(OH)_2$.....	2.0	7.4	0.0212	none	none		
$Ca(OH)_2$.....	4.0	7.5	0.0155	none	none		
$Ca(OH)_2$.....	8.0	8.0	0.0085	none	none		
MgO.....	2.0	7.4	0.0197	none	none		
MgO.....	4.0	7.7	0.110	none	none		
MgO.....	8.0	8.1	0.0094	none	none		

Another deviation is that, on the anionic side, there seems to be a maximum, the silica showing a tendency to decrease at the highest pH. This would be in harmony with the known peculiarity of silica sol to form a gel, or to precipitate most easily at a pH slightly above the neutral point.

To illustrate what has been said in the last two paragraphs, an older, but unpublished, experiment with electrodialyzed Ancylus clay will here be included. Samples of 25 gm. clay were shaken for 36 hours in 500 cc. of water, in the presence of HCl, NaOH, $Ca(OH)_2$, and MgO. The suspensions were then filtered through Pasteur-Chamberland filters, the pH was determined colorimetrically, and 400 cc. of the filtrate was analyzed with the result shown in table 150.

The following points are of interest in connection with the present investigation:

Silica has a minimum somewhere above pH 8.

The solubility of silica does not seem to be markedly influenced by the nature of the base.

No Al and Fe is carried in solution by silica.

Silica is carried in solution by the sesquioxides, resulting in an apparent increase in the solubility of silica with a decrease in pH, but,

The SiO_2/M_2O_3 ratio decreases rapidly with a decrease in pH. Therefore,

Since the loss of silica dominates above a certain pH, and the loss of sesquioxides dominates below this pH, leading to an enrichment of the soil in sesquioxides in the first case, and an enrichment in silica in the second case, we get an isoelectric weathering in the case of the silicate gel complex as in the case of the humate gel complex.

The Al_2O_3/Fe_2O_3 ratio increases with a decrease in pH. This means that Fe is relatively more soluble than Al at the higher pH. This we ascribe to the ferrous form of iron, in this case, where we are dealing with a slightly weathered glacial clay. In podzolization, iron is the first to become mobile (12). Where we have ferrous iron this must be so, because the ferrous compounds have a higher isoelectric point than the corresponding compounds of Al and ferric iron, and must, therefore, be the first to become cationically dispersed.

It is interesting to note that the glacial clay, from which 26 m.e. of base, per 100 gm., had been removed by electrodialysis, yielded an extract with a pH of 7.3 after 36 hours of shaking in pure water. Immediately after the electrodialysis, the clay had a pH of 4.2. This "rock flour" will not long remain "unsaturated." It mobilizes new capital by drawing upon the principal, stored up in the vaults of the crystal lattices.

In figure 60, we have graphically represented the composition of the isoelectric precipitates in relation to the isoelectric pH. The points are a little scattered, but the increase in the acidoid/basoid ratio with a lowering of the isoelectric pH is clear enough. It must be remembered that these systems are more complex than the corresponding systems of "pure" humates and silicates, represented in figures 44 (*b*) and 47 (*b*), respectively (10). There are here other acidic and basic constituents than humus, silica, and sesquioxides. Among the other materials present, phosphoric acid, titanium, manganese, and ferrous iron might be mentioned. These all affect the isoelectric point. Then it must be pointed out that all the errors of the different procedures are here brought together. Chief among these are the errors involved in electrophoresis. These are generally large and due to various causes. Then, the composition of the extract, which is largely colloidal, might vary considerably because of variations in the permeability of the filters, as affected by the different mixtures. Some filtered slowly, others more or less rapidly.

In figure 61 we have plotted the humus/sesquioxide ratios in the extracts of the various series against the pH of the extracts. We have then inserted the

upper curve in figure 60, representing the isoelectric composition with respect to the same ratio (broken line). The points at which this curve intersects, or would interesect if extrapolated, the other curves correspond to the minima in

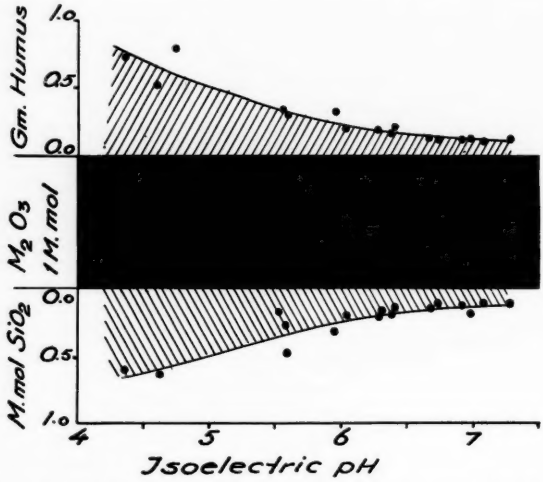


FIG. 60. The relation between the isoelectric pH and the composition of the extracts, expressed in millimols silica and grams organic matter (humus) per millimol sesquioxides.

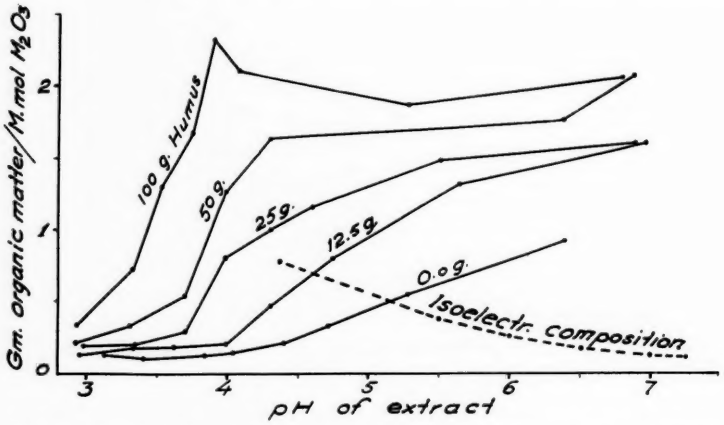


FIG. 61. The relation between the ratio of organic matter to sesquioxides and the pH of the extracts. The broken line shows the isoelectric composition (cf. fig. 60).

figure 56 and represent the isoelectric points of the gel complex in the different mixtures.

The curve is also a dividing line between the cationic and anionic sol complex.

All points on the other five curves which lie below this curve are on the acid side of the isoelectric point of the gel complex. The sol complex is, therefore, here cationic. The isoelectric point of any cationic sol complex is found by drawing a horizontal line to the right until it meets the broken line. All points which lie above the intersecting curve are on the "alkaline" side of the isoelectric point of the gel complex. The sol complex is, therefore, here anionic. The isoelectric point of an anionic sol complex is found by drawing a horizontal line to the left until it meets the broken line. This is, however, possible only within certain limits, because, according to the aforementioned anomaly (10), a humate complex in which the proportion of humus exceeds a certain value remains anionic even at low pH. The intersecting curve does not, therefore, continue indefinitely to the left.

THE RÔLE OF THE SOL COMPLEX IN SOIL FORMATION

If we calculate the molar ratios of silica to sesquioxides in the lithosphere on the basis of the data supplied by Clarke (2, p. 31) we get

$$SiO_2/Al_2O_3 = 5.44, \text{ and } SiO_2/Al_2O_3 + F_2O_3 = 4.27$$

The ratios are for the silicate silica only, the 12 per cent assumed to be quartz being subtracted, and FeO is calculated as Fe_2O_3.

We note that the ratios are very high. The isoelectric point of the gel complex which is formed from the products of hydrolysis of the igneous rocks must, therefore, be very low. This is especially true in the case of the soil where the gel complex contains humus in addition to silica as a dominantly acidic constituent. Since the lithosphere contains large quantities of the strong bases (there are 1.45 mols of CaO, MgO, K_2O, and Na_2O, combined, per mol sesquioxides) which become liberated, we would expect the pH of the soil to stay above the isoelectric point of such a complex. This is also, normally, the case, except under special conditions, such as those leading to the formation of large quantities of organic and inorganic acids, to be discussed below.

A pH above the isoelectric point of the gel complex will give rise to a sol complex which is anionic and, therefore, richer in acidoids than the parent gel, whereas the latter will become richer in basoids and increase its isoelectric pH as the leaching proceeds. This must continue until the latter pH and the pH of the soil coincide. At this point the dispersed material has the same acidoid/basoid ratio as the parent gel complex. The position of this point will depend to a large extent on the magnitude of the humic constituent, which is maintained in the gel complex, and which is governed by various factors. Where the humus content is high, the isoelectric point remains always low, but where there is little humus in the complex, its isoelectric pH will increase, with the progressive loss of silica, until the lateritic stage is reached.

That the process of weathering in the humid regions proceeds according to the above postulate is shown by the composition of soil colloids. The analyses of Robinson and Holmes (13), covering 45 soil colloids from various parts of

the United States, show an average ratio of silica to sesquioxides of 2.18. This figure becomes considerably lower if the colloids from arid regions are eliminated. The soil colloids are richer in sesquioxides and poorer in silica and bases than the original rock.

The above type of weathering, which might be termed *anionic solvation and eluviation*, is the type which leads to the formation of laterites, red, yellow, and brown earths, and brown forest soils.

In a previous publication (11), it was stated that the anionic sol complex cannot be isoelectrically precipitated during its downward movement in a soil, the pH of which increases with the depth, because the ionization and negative charge of the complex will be greater only as the pH increases. But it may, nevertheless, be precipitated, not by the OH ions, but by interaction with the gel complex, which in the deeper B horizon has a higher isoelectric point than the gel complex in the upper A, or humus, horizon. The gel complex in B will then act as a base toward the more acidic sol complex, coming from the A horizon. Thus, it has been found that dark-colored electronegative sols may be nearly decolorized by passing through soil material from the B horizon of a brown soil, as well as of a podzol profile. This type of precipitation is responsible for the chemical illuviation of acidic material, traceable in the non-podzolic profiles, notably the impregnation of organic matter in the deeper horizons (4). But a large part of the anionic sol complex reaches the streams and rivers. It is largely material of this nature which imparts a brownish color to their water. The harder well water is clear, because the negative sol is flocculated by the Ca ions.

The anionic solvation and eluviation leads to an increase in the isoelectric pH of the gel complex. The leaching of the bases leads to a decrease in the pH of the soil. When the two pH values coincide, that is, when the net base saturation of the complex is zero, the step to the other type of weathering, i.e., the *cationic solvation and eluviation*, is a short one. If the production of acids exceeds the production of bases, as under conditions of the formation of a sour humus cover, then the pH of the soil will fall below the isoelectric pH of the complex. The exchangeable cations being practically exhausted, the basic residue of the complex will become engaged, and a cationic sol complex will be mobilized, resulting in a development of the podzol profile. The cationic sol complex, being richer in basoids, will leave the gel complex richer in acidoids and with a lower isoelectric point. The lowering of the isoelectric pH will tend to oppose a further cationic solvation, just as an elevation of the isoelectric pH tends to oppose a further anionic solvation (Le Chatelier's law).

Since the pH in the soil normally increases downward, the cationic sol complex, unlike the anionic complex, is always isoelectrically precipitated at a certain depth in the soil, giving rise to the B horizon of the podzol profile. The depth at which the cationic complex will precipitate will, of course, depend upon its isoelectric point, and upon the pH gradient in the profile.

We have deep, and we have shallow, podzol profiles. A podzol profile at

Sunnersta near Uppsala, having a high water table and glei formation at 17 cm., had a pH of 3.9 at 10 cm., and 5.2 at 17 cm. The B horizon is dark brown, compact with some ortstein, but only about 4 cm. deep. Where the pH gradient is less steep, the cationic sol complex can wander to a considerable depth, if its isoelectric point is high.

According to Aaltonen (1), precipitation takes place at a greater depth in the younger than in the older podzols, that is, the B horizon grows from the bottom up. This should mean that the isoelectric point of the cationic sol complex is higher in the former than in the latter. The isoelectric point of the cationic sol complex will be determined by the pH of the soil, and by the isoelectric pH of the gel complex, as shown in the experimental part (cf. figs. 55 and 61). In the early stages of the process of podzolization, while the gel complex in the A horizon is still relatively rich in sesquioxides, we would expect the isoelectric point of the cationic sol complex to be higher and the complex to wander deeper than in the older podzols. Later, as the sesquioxides become exhausted, the isoelectric point of the sol complex will be lower, and will, accordingly, be precipitated by the lower pH in the upper B horizon. Our theory will, therefore, not only give a satisfactory explanation of the fact that the material precipitated in the upper B is more acidic than that precipitated in the lower part of this horizon; it will also explain "das Aufsteigen des B-Horizontes nach oben beim Älterwerden des Bodens" (1).

If the podzol B horizon grows from the bottom up, as claimed by Aaltonen, where, and by what, is it stopped? Is there then a lower limit to the A horizon?

We shall attempt to answer the questions on the basis of the laws of isoelectric precipitation and of the present status of our experimental work. The cationic solvation and eluviation proceeds downwards from the top of the mineral soil,[2] whereas the precipitation begins at a certain depth, depending upon the pH, and proceeds upwards, as the cationic sol complex becomes more and more acidic with the age of the profile.[3] The "waves" will ultimately meet, that is, the zone of precipitation will border on the zone of solvation. At this stage, the cationic sol complex has become so acidic, and its isoelectric point so low, that it is precipitated at a pH immediately below that prevailing in the lowest part of the A horizon. This marks the upper limit of the B horizon. When the isoelectric pH of the gel complex in the A horizon has been reduced to a value equal to the prevailing pH in this horizon, there can be no further mobilization of a cationic complex; where the crest of precipitation coincides with the valley of solvation, there is no motion.

The process, as described, is illustrated in figure 61. Let us assume a pH of 4 in the zone of eluviation, and let series I (0.0 gm. humus) represent the condi-

[2] Because of a high humus content in A_1, the solvation of sesquioxides is usually less intense in A_1 than in A_2 (3).

[3] The composition and properties of the sol complex will also vary with the seasonal fluctuations in humus formation, pH, rainfall, etc.

tions at the beginning. The cationic sol complex would be isoelectric at about pH 7, and would be precipitated at a depth in the profile where the pH is, let us say, about 6. Later, as the gel complex in the A horizon becomes more acidic, the conditions will be more nearly represented by series II (12.5 gm. humus). The isoelectric pH of the cationic sol complex is then about 6 and would be precipitated at a depth in the profile where the pH is, let us say, about 5. Now let series III (25 gm. humus) represent the conditions at an advanced stage of podzolization. The isoelectric pH of the cationic sol complex is only slightly above 4, or at about 4.2. This complex, if it were formed at all, would obviously be precipitated by the slightest increase in pH, or immediately under the zone of eluviation. A slightly more acidic system would itself be isoelectric at the assumed pH of 4, and this would mean an end to the cationic solvation and eluviation in the A horizon.[4]

The result of a still further increase in the acidoid content in the soil complex in the A horizon, through an increment of humus, is illustrated by Series IV (50 gm. humus) in figure 61. The isoelectric pH of the complex will be lower than the pH of the soil, and the preceding cationic solvation and eluviation will be succeeded by an anionic solvation and eluviation. The anionic sol complex will, however, to a large extent be precipitated in the B horizon, in combination with the more basic gel complex there. This precipitation of primarily humic material would proceed from the upper to the lower parts of the B horizon, and would represent the beginning of the formation of the "humus podzol."

The process might also be illustrated by a direct application to the podzol profile, as in figure 62, which is taken from the previously mentioned work (11). The figure shows the average actual (pH_o), and ultimate (pH_u), pH in the different horizons of eight podzols as described in an earlier publication (8). The fact that pH_u is higher than pH_o in the B and C (or lower B) horizons was then explained as depending on the precipitation of the complex in its cationic condition, that is, in the condition of a partial saturation with acids and in the condition of practical unsaturation with bases. When this is the case, the precipitated material must have a higher pH after the diffusible acids have been removed by electrodialysis.

Let the size of the minus and the plus circles represent the relative magnitude of the negative and positive charges of the amphoteric soil complex. Suppose now, that, at the beginning of the process, when the soil is rich in sesquioxides, the conditions in the A_2 horizon, where the pH is 4.01, be such that a complex *a*, isoelectric at 5.2, is mobilized. This complex, which exists in a medium, the pH of which lies a considerable distance below its isoelectric point, would carry a strong positive charge and remain mobile down to, let us say, the lower

[4] The pH might, of course, sink below 4 and keep the process going, but only for a limited length of time, because there is a limit to the amount of sesquioxides present in the complex, and then there must likewise be a limit to the acidity produced by the leachings from the humus layer. The ultimate state would, therefore, be the same.

part of the B horizon, or a' in the figure. If after a partial depletion of sesquioxides, the conditions be such that a complex b is mobilized, which has a lower isoelectric point, e.g., at 4.8, then the charge will be lower, and the complex will be precipitated at a lower pH or, let us say, in the middle part of the B horizon, or at b' in the figure. Again, if, at an advanced stage of leaching, a complex c, isoelectric at 4.4, be mobilized, the precipitation would take place at a still lower pH, at, let us say, a point c', still higher up in the B horizon.

A complex isoelectric at, or near, pH 4.01 could not become mobile but would remain in the gel condition.

If the isoelectric point of the mobilized complex should be lower than the pH of the A_2 horizon, then the complex will carry a negative charge, and this charge will increase with the pH in the lower horizons. Such complexes, as exemplified by e and d in the figure, will not precipitate *isoelectrically* in the

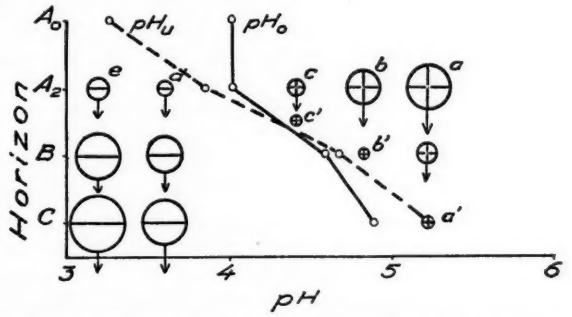


FIG. 62. A scheme to illustrate why the cationic sol complex, which is mobilized in the A_2 horizon of the podzol profile, must be isoelectrically precipitated at a certain depth in the B horizon before a pH, corresponding to the isoelectric point, is reached (plus circles); and why an anionic complex cannot be isoelectrically precipitated since its negative charge increases downward as the pH increases (minus circles). Each point plotted represents the average of eight podzol profiles; pH_0 is actual pH, and pH_u is ultimate pH.

podzol profile where the pH tends to increase. They may, however, be precipitated by combining with the more basic gel complex in the B horizon, as above indicated.

The scheme in figure 62 was not used originally to illustrate the development of the podzol in relation to age. It was used to account for the fact that the gel precipitated in the upper B horizon is more acidic than the gel in lower B. We note that the theory fits both cases equally well.

We now come to the question of the lower limit of the A horizon.

With the continued production of acids in excess of bases, it seems obvious to us that the eluviation of sesquioxides must continue down into the B horizon. For, if these acids are not "neutralized" in the A horizon, because of the lack of basic material, and if they are not decomposed on their way, they will pass on to the B horizon and there ionize the sesquioxides once precipitated.

If the B horizon is poor in humus, as in the case of the drier profiles (*iron podzols*), then the bleached horizon would simply extend downwards. But in the case of the wetter profiles, in which there is a high humus content in the B horizon, a part of the humus in combination with Al and Fe would be set free and, as a colloidal acid, left behind. The color would, therefore, be dark gray to black in this case. The chemical nature of this reaction would, however, be the same as in the case of the upper bleached layer of the A horizon, to which the cationically eluviated, but blackish, layer genetically belongs. The process would lead to the development of the humus podzol.

Below the layer of humus accumulation, a second bleached layer might develop after the eluviation of the sesquioxides. Due to the high isoelectric point, the cationic eluviation in this layer might precede the eluviation in the humus layer higher up. This second bleached layer would correspond to the Ba_2 horizon described by Tumin (15).

All of these layers, the humus dark as well as the bleached layers, belong to the cationically solvated and eluviated, or podzolized, horizon. It is, therefore, not merely a question of color and of eluviation and illuviation when the podzolized horizon is to be defined. The kind of material involved, whether acidic or basic, is more important. The process of podzolization cannot be clearly defined without a distinction between anionic and cationic solvation and precipitation. We shall return to a discussion of this problem later in connection with our present work on humus podzols.

Aaltonen found a periodic precipitation of iron when he precipitated a ferric hydroxide sol in columns of sand and states that this cannot be explained on the basis of isoelectric precipitation. But the isoelectric precipitation is to a certain extent autocatalytic (7). It must be remembered that a cationic sol is precipitated, already, on the acid side of its isoelectric point, especially when combining with a colloid having a lower isoelectric point, e.g., the gel complex in the sand. The initial precipitation will serve as a nucleus for a further precipitation, because the isoelectric pH of the silicate (or humate) complex, being increased through the addition of basoid, will cause the pH of the medium to be higher in the immediate neighborhood of the complex, thus rendering the sol more unstable. We look upon such zones of a higher pH as the cause of the formation of concretions and of the horizontal streaks observed by Tamm (14) in the B horizon of undeveloped podzols.

SUMMARY

The anionic and cationic sol complex, obtained at different pH in the extracts from various mixtures of soil and humus, has been studied with respect to composition and isoelectric point.

It has been found that there is a minimum of solvation at a pH which corresponds to the isoelectric point of the gel complex in the mixture.

Above this pH, the sol complex is anionic and more acidic than the gel complex, whereas it is cationic and more basic than the latter at lower pH.

Applied to the process of soil formation, a distinction is made between anionic solvation and eluviation leading to laterites, red, and brown earths, and cationic solvation and eluviation leading to podzolic soils.

REFERENCES

(1) AALTONEN, V. T. 1935 Zur Stratigraphie des Podsolprofils I. *Communicationes Instituti Forestalis Fenniae*, 20.6: 5–150.

(2) CLARKE, F. W. 1920 The Data of Geochemistry, ed. 4, Washington, D. C.

(3) JOFFE, J. S. 1936 Pedology. Rutgers University Press, New Brunswick, N. J.

(4) LUNDBLAD, KARL 1934 Studies on podzols and brown forest soils: I. *Soil Sci.* 37: 137–155.

(5) MATTSON, SANTE 1928, 1933 Cataphoresis and the electrical neutralization of colloidal material. *Jour. Phys. Chem.* 32: 1532–1552 (1928); Cataphoresis. An improved cylindrical cell. *Jour. Phys. Chem.* 37: 223–227 (1933).

(6) MATTSON, SANTE 1930, 1931 The laws of soil colloidal behavior: III. Isoelectric precipitates. *Soil Sci.* 30: 459–495 (1930); IV. Isoelectric precipitates. *Soil Sci.* 31: 57–77 (1931).

(7) MATTSON, SANTE 1933 The Laws of soil colloidal behavior: XI. Electrodialysis in relation to soil processes. *Soil Sci.* 36: 149–163.

(8) MATTSON, SANTE, AND GUSTAFSSON, Y. 1934 The chemical characteristics of soil profiles: I. The podzol. *Ann. Agr. Col. Sweden.* 1: 33–68.

(9) MATTSON, SANTE, AND GUSTAFSSON, Y. 1935 The chemical characteristics of soil profiles: II. The mutual interactions of podzolic materials. *Ann. Agr. Col. Sweden.* 2: 1–30.

(10) MATTSON, SANTE, AND GUSTAFSSON, Y. 1937 The laws of soil colloidal behavior: XVIII. Colloidal electrolytes. *Soil Sci.* 43: in press.

(11) MATTSON, SANTE, AND NILSSON, I. 1935 The chemical characteristics of soil profiles: III. The podzol complex. *Ann. Agr. Col. Sweden.* 2: 115–134.

(12) MUIR, ALEX. 1934 The soils of the Teindland state forest. *Jour. Soc. Foresters Gt. Brit.* 8: 25–55.

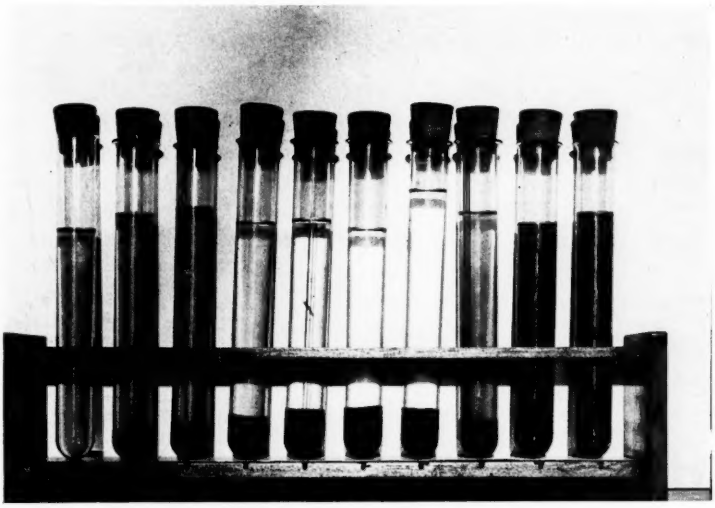
(13) ROBINSON, W. O., AND HOLMES, R. S. 1924 The chemical composition of soil colloids. U. S. Dept. Agr. Bul. 1311.

(14) TAMM, OLOF 1920 Markstudier i det nordsvenska barrskogsområdet. Meddel. Statens Skogsförsöksanst. [Sweden]. 17: 49–300.

(15) TUMIN, G. M. 1912 A survey of the general character of soil morphology and its changes within the zones. *Zhur. Opuit. Agron.* 13: 321–353. (Cited from Joffe's Pedology (3).)

PLATE 3

THE ISOELECTRIC PRECIPITATION OF A CATIONIC SOL COMPLEX (SEE TABLE 148)



NOTE ON ACCURACY OF SOIL THERMOGRAPHS

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In a recent paper (2) in this journal, the accuracy of the soil thermograph was discussed, and certain precautions were noted which contribute to greater accuracy of such readings. The thermograph discussed had a bulb 12 inches long and $1\frac{1}{16}$ inches in diameter, with 10 feet of copper braided tubing between the bulb and the expansion chamber and recording needle. The discussion was concerned with records obtained at shallow depths. Two possible errors were noted: (*A*) that caused by the sharp temperature gradient in the space ($1\frac{1}{16}$ in.) occupied by the bulb when near the soil surface, and (*B*) that caused by conduction of heat along the copper braided tubing to the sensitive bulb. It was recommended that about 3 feet of the tubing be buried at the same depth as the bulb, so that the second source of error would be eliminated.

At the Desert Laboratory, Tucson, Arizona, we have had some interesting experiences with these thermographs, the bulbs of which were buried at greater depths, down to 12 feet (1). I should like to point out a further precaution which is especially significant when dealing with the lower levels of the soil.

From other methods of measuring temperatures, we knew that no diurnal variation occurred at the 3-foot depth and below. Yet, a thermograph with the recording end in a wooden box exposed to the free air and with the bulb 6 feet deep exhibited a diurnal variation of from 1°F. to 3°F. The recording end of the instrument, including, of course, the expansion chamber, was thus subjected to a diurnal range of air temperature of about 40°F. normally. When the recording mechanism was placed in an insulated compartment, in which there occurred only small daily temperature variations, no variation was noted on the thermograph chart. The conclusion appears to be that the expansion chamber must be protected from extremes of temperature. When heat was applied to the expansion chamber, the thermograph's recording pen indicated a fall and, conversely, when the chamber was cooled, the pen indicated a rise. Throughout the test, the temperature around the bulb itself did not change. Diurnal changes of less than 10°F. around the expansion chamber did not produce any variation in the record made by the recording pen.

Our procedure is to keep the recording end of the thermograph in a small cellar where very small daily changes in temperature occur. We attempt throughout the year to keep the temperature around the tubing and around the recorder at figures fairly close to that of the bulb.

The inference is very strong that this "expansion chamber error" will cause readings at shallow depths to be somewhat inaccurate if the chamber is exposed to the diurnal variations in air temperature, the minimum reading being somewhat too high and the maximum too low.

REFERENCES

(1) Carnegie Inst. Wash. 1936 Report Div. Plant Biol. Yearbook No. 35:219.
(2) MAIL, G. ALLEN (1937) Accuracy of a Soil Thermograph. *Soil Sci.*, 43:27–30.

BOOK REVIEWS

Rasteniya Polevoi Kultury (Field Crops). By D. N. PRYANISHNIKOV and I. V. YAKUSHKIN. (Chastnoe Vemledelie, Ninth Edition.) Selkhozgiz, Moscow, 1936. Pp. 843.

The first edition of this work, prepared under the direction of Prof. Pryanishnikov, appeared in 1898. The eighth edition of the present work appeared in 1931. Since 1898, the material for the present edition has been gradually amplified, and various gaps have been filled in. The authors admit that, under the compulsion of condensation, they were obliged to treat some important crops rather sketchily.

The treatise is made up of seven parts, dealing, respectively, with the cereal grains, seeds rich in protein, seeds containing a high percentage of oil, tuber crops, root crops, fiber crops, and forage crops. The first division includes not only such small grains as rye, wheat, oats, and barley, but also buckwheat, millet, Indian corn, sorghum, and rice. In the second division, crops like field peas, horse beans, lupines, soybeans, and peanuts are dealt with in considerable detail. Among the crops whose seeds are rich in oil, the authors discuss sunflower, sesame, rape, etc. There is also included in this division a discussion of such crops as mustard, anise, coriander, and fennel. Potatoes are dealt with in considerable detail in Section 4. In the following section, sugar beets, chicory, fodder beets, carrots, turnips, etc. are considered. Flax, cotton, hemp, and jute occupy most of the space in Section 6. Among the forage plants, the authors discuss at some length clover, alfalfa, timothy, vetches, rye grass, Sudan grass, etc. An extensive list of references, particularly those relating to experiments and observations in the U. S. S. R., is supplied by the authors.

In view of the rapid expansion of areas devoted to field crops in the Soviet Republics and the new methods employed in growing these crops, the book should be found valuable for reference purposes.

Fundamentals of Qualitative Chemical Analysis. By ROY K. MCALPINE and BRYON A. SOULE. D. Van Nostrand Company, Inc., New York, 1936. Pp. ix + 325, tables 12.

The purpose which guided the authors in writing this book is indicated in the preface. They say:

> In the present text an attempt has been made to provide more specific assistance than usual for both the teacher and the student. Through the systematic development of the groups in the analytical scheme according to a well defined plan, it is possible to use the book effectively for a satisfactory correlation of class and laboratory work.

They say further:

> Several other features of the book deserve brief comment. First, each set of laboratory exercises starts with a series of known solutions to be analyzed. It is the conviction of the authors that the laboratory period is essentially a time for study rather than for being tested on analytical ability.

The book is made up of a preface, 17 chapters, an appendix, logarithms, and an index. The several chapters are designated, respectively: Introduction; Chemical Arithmetic; Formulas and Equations; Ionization Theory in Analytical Processes; Introduction to Laboratory Work; Group I, Lead, Silver, Mercury; Study Aids; Copper Division of Group II; Group III, Iron, Chromium, Aluminum; Group IV, Zinc, Manganese, Cobalt, Nickel; Group V, Barium, Strontium, Calcium; Group IV, Magnesium, Sodium, Potassium, Ammonium Radical; Arsenic Division of Group II; More Common Acid Radicals; Other Common Acid Radicals; Simple Dry Unknowns; and Complex Dry Unknowns.

The rather far-reaching changes in our definitions and interpretations of chemical processes have been recognized by the authors in the preparation of this volume. It should be commended as a satisfactory and convenient textbook for the study of qualitative chemical analysis.

Annual Survey of American Chemistry. Volume X, 1935. Edited by CLARENCE J. WEST. Published for the National Research Council by Reinhold Publishing Corporation, New York, 1936. Pp. 487. Price $5.00.

The editor and his associates have made another valuable contribution to the progress of chemical education and research in the United States. The editor notes in his foreword, that

> With this volume, the Annual Survey completes the first decade of its existence, the ten volumes covering the period 1925 to 1935, inclusive. During this time an endeavor has been made to cover, as completely as possible, the progress made in American Chemistry, and to indicate, by implication if not by actual statements, the trends in the various fields of pure and applied chemistry in the United States.

The following is a list of the topics considered in the 25 chapters: Theories of Solution—Herbert S. Harned and Benton B. Owen; The Kinetics of Homogeneous Gas Reactions—F. O. Rice and K. F. Herzfeld; Molecular Structure—E. Bright Wilson, Jr.; Thermodynamics and Thermochemistry—R. E. Gibson; Contact Catalysis—L. H. Ryerson; Inorganic Chemistry, 1933–35—Don M. Yost; Analytical Chemistry, 1934 and 1935—G. Frederick Smith; Applications of X-Rays in Metallurgy—Eric R. Jette; Ferrous Metallurgy—Frank T. Sisco; The Platinum Metals—Raleigh Gilchrist; Electro-organic Chemistry—Sherlock Swann, Jr.; Aliphatic Compounds—M. S. Kharasch and C. M. Marberg; Carbocyclic Compounds—W. E. Bachmann and F. Y. Wiselogle; Heterocyclic Compounds—Guido E. Hilbert; Alkaloids—Lyndon Small;

Food Chemistry—Caroline C. Sherman and Henry C. Sherman; Insecticides and Fungicides—R. C. Roark; Gaseous Fuels, 1934 and 1935—Lloyd Logan and Wilbert J. Huff; Petroleum Chemistry and Technology—Merrell R. Fenske; Detergents and Detergency—Pauline Berry Mack; Cellulose and Paper—Harry F. Lewis; Synthetic Plastics—Gustavus J. Esselen and Walter M. Scott; Rubber—Webster N. Jones; Unit Processes in Organic Synthesis—edited by P. H. Groggins; and Chemical Economics (1931–1935)—Lawrence W. Bass.

There is scarcely any important phase of chemistry that has been overlooked. The theoretical, as well as the applied sides, of a broad subject have received competent treatment. On the applied, the reader will note with satisfaction the discussion of progress in metallurgy, food processing, fuels, cellulose, synthetic plastics, and rubber.

The reviewer is tempted to quote a short paragraph from Chapter 25 on Chemical Economics (1931–1935) by L. W. Bass. He says:

> It is safe to prophesy, however, that eventually a rounded philosophy of chemical economics will be evolved through mutual effort of the chemist and the economist. It is the writer's hope that this survey of the literature may stimulate that progress and mark a milestone on the road.

The book contains a wealth of reference material. The editor and his associates have placed many investigators and teachers under debt to them.

Handbuch der Landwirtschaftlichen Bakteriologie. By F. Löhnis. Gebrüder Borntraeger, Berlin, 1933. Part I, pp. 158; Price 10.50 RM. Part II, pp. 105; Price 15 RM.

Through an oversight on the part of the reviewer, this publication by the late F. Löhnis was not presented to the readers of SOIL SCIENCE at an earlier date. The information contained in this book is of more than usual interest and value, and the reviewer, with due apologies, wishes at this late date to bring the contents of the Handbuch to the attention of the readers of this journal.

Volume I (F. Löhnis, Futtermittelbakteriologie) of this work treats of the presence and activities of microorganisms in forage crops. Volume II (G. Ruschmann, Düngerbakteriologie) deals with the presence and activities of microorganisms in animal manures.

The authors have rendered a distinct service by summarizing up to 1933 all the studies on the subjects referred to. The numerous references given by them cover a wide range of publications in different countries. They have considered not only the investigations more or less familiar to the student of agricultural bacteriology, but have given thought also to the less accessible publications. To that extent, they have rendered more than an ordinary service to students of soil microbiology.

The Principles of Bacteriology and Immunity. By W. W. C. TOPLEY and G. S. WILSON. William Wood and Company, Baltimore, 1936. Pp. xv + 1645, tables 192, figs. 274. Price $12.00.

In their preface to the first edition, the authors pointed out that

> It has become increasingly evident, during the past ten years, that there is a need for the provision of organized teaching in the principles and technique of bacteriology, of a far more detailed and extensive kind than can be included within the four corners of an overcrowded curriculum, or in the scarcely less crowded courses of post-graduate study which lead to a Diploma in Public Health, in Tropical Medicine and Hygiene, or in Veterinary State Medicine. There is an increasing demand, at home and abroad, for the services of the trained bacteriologist; and it is no longer possible, or justifiable, to meet this demand by trusting to the emergence of a certain number of bacteriologists, as a by-product of a training designed for those whose work in life will lie in the clinical or administrative field.

The first edition appeared in 1929. There is, therefore, a gap of seven years between the first and second editions. In their preface to the latter, the authors say:

> The seven years that have elapsed since the publication of the first edition of this book have witnessed a rapid advance in the science of bacteriology—more rapid, perhaps, than any that has occurred since its early infancy. As a consequence, the task of revision has been peculiarly difficult. Adequate reference to all the new knowledge that has been acquired would have entailed expansion to a size altogether inappropriate to a textbook of this kind; and we have been compelled to push selection very far.

In the light of the authors' statement, the reader must consider sympathetically the effort that they have made to deal with a field of knowledge vast in itself and constantly changing. The four parts are devoted, respectively, to General Bacteriology, Systematic Bacteriology, Infection and Resistance, and The Application of Bacteriology to Medicine and Hygiene. There is a total of 89 chapters in the book and an index of 43 pages.

The book may be commended to the teacher, investigator, student, and to practitioners in various fields of applied bacteriology. They will find profit and satisfaction in the wealth of scientific data and reference to published work.

Applied Dietetics. By FRANCES STERN. The Williams & Wilkins Company, Baltimore, Md., 1936. Pp. xxi + 263, tables 52.

In these days of family budgets, there is danger of underestimating the significance of the food factor in the well-being of the individual and the family. We are inclined to over-estimate the value of the claims made by various faddists who may be telling us about minerals, vitamins, ultraviolet rays, and what not, as relating to the important subject of human nutrition. The need for more authoritative and sound books on the subject of dietetics is more pronounced than it ever has been. The present work should, therefore, be welcome as an acceptable contribution in a field of wide interest.

The author notes in the introduction that

> For the person who is unfamiliar with the necessary data and the procedure in diet planning, a *text* has been written, stating the underlying principles and demonstrating the use of the tables and outlines. Each step in the construction of a diet is explained and reference is given to related tables. With experience a diet can be evaluated, in terms of the kinds and amounts of food necessary to fulfill the food prescription, accurately enough for clinical use without actually computing it.

The book is divided into four parts. Part I contains six chapters, entitled: The Daily Food Requirements of the Body; The Construction of the Normal Diet; The Construction of the Therapeutic Diet; Environmental Factors that Influence the Effectiveness of the Diet; The Education of the Parent on the Normal Diet; and The Education of the Patient on the Therapeutic Diet. Part II contains 52 tables, arranged to simplify the computation of the diet. Part III deals with diets from the point of view of various human ailments. Part IV covers typical diets and menus.

The author has succeeded in arranging the material effectively and, in general, has provided a treatise which will prove widely helpful and useful.

JACOB G. LIPMAN.

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